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TECHNICAL NOTES

No. 7. A STUDY ON CONTRACTION, RELATIVE VISCOSITY AND MELTING CURVES OF SOME GLASS-FORMING HYDROCARBON MIXTURES
By Kj. Rosengren

No. 8. SOME NEW GLASS-FORMING HYDROCARBON MIXTURES
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No. 9. A SYSTEMATIC STUDY OF THE PHOTOLYSIS OF SOME DIALKYL DISULFIDES IN A RIGID GLASS AT 77°K
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No. 11. THE PHOTOLYSIS OF IODINE, ETHYL IODIDE AND HYDROGEN IODIDE IN A RIGID GLASS AT 77°K
By D. Timm

CATALOGED BY ASTIA AS AD No.

Thermochemistry Laboratory,x) University of Lund, Lund, Sweden

15 January 1962

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TECHNICAL NOTE

A STUDY ON CONTRACTION, RELATIVE VISCOSITY AND MELTING CURVES OF SOME GLASS-FORMING HYDROCARBON MIXTURES

By

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ABSTRACT: The contraction, relative viscosity and melting curves have been studied for a number of hydrocarbon mixtures that form glassy states upon freezing at 77°K. The commonly used *iso*-pentane - 3-methyl pentane glasses as well as three new mixtures have been stud'ed.

INTRODUCTION

During the course of an investigation of the photolysis of organic substances in a rigid matrix at liquid nitrogen temperature it was felt desirable to study, quantitatively, the following properties of the different glass-forming mixtures: the specific volume ratio between 298° and 77°K; the rigidity of the matrix as a function of temperature, and the melting behaviour of the matrix. The contraction of the mixture must be known in order to convert concentration values from room temperature to 77°K. The viscosity of the matrix has a marked influence upon the photolysis path[1,2] but has, so far, not been quantitatively estimated as a function of temperature. Finally, the heating curve of a particular matrix mixture reveals the possible existance of microcrystalline structures in the glass at 77°K or the formation of crystals during warm-up.

The following glass-forming mixtures have been studied:

3-methyl pentane (pure)[1]
iso-pentane - 3-methyl pentane (6:1)[x) 3]
iso-pentane - 3-methyl pentane (2:3)[1]
n-pentane - neo-hexane (3:8)[4]
3-methyl pentane - methyl cyclohexane (1:2)[4]
3-methyl pentane - methyl cyclohexane (1:6)[4]

MATERIALS

All hydrocarbons were Phillips Petroleum Company "pure" grade hydrocarbons, except iso-pentane and 3-methyl pentane, which were "technical" grade samples from the same company. They were all purified by a routine method, which, in principle, is described in the literature[5].

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x) Volume ratios are given.

After the hydrocarbon (about 2 l) had been treated with concentrated sulphuric acid for five hours, it was neutralized, washed with water and dried over night with "Drierite". The liquid was refluxed over sodium wire, transferred to a still pot, freshly prepared sodium wire was added and the sample was carefully distilled in a 35 plate all glass column packed with Fenske helices; reflux ratio 1:30, 150-200 ml being collected every 24 hours. From these fractions samples were withdrawn and analyzed on a gas chromatograph (Pye Argon Chromatograph Type 12000) with dioctyl phthalate as stationary phase. For n-pentane and neo-hexane all fractions which contained more than 0.05 % impurities were discarded, for cyclohexane the corresponding figure was 0.1 %. i-Pentane was allowed to contain max. 0.5 % n-pentane and for 3-methyl pentane max. 1 % 2-methyl pentane was allowed.

Samples from those fractions which passed the gas chromatographic analysis were tested for ultraviolet transmission below 50 kc. cm^{-1} in a spectrophotometer (Beckman DU equipped with a photomultiplier), and fractions exhibiting a transmission appreciable lower than the pure compound were recycled.

The pure fractions were brought together and allowed to pass a glass column (60 × 2.5 cm) packed with Davidson No. 200 mesh silica gel. The silica gel had been activated in the tube at 350°C. In order to remove the last traces of water, the silica gel tube was evacuated to 1 mm of Hg at 350° and then allowed to cool in vacuum. After the silica gel treatment the ultraviolet transmission was checked again. It was found that a second treatment with fresh silica gel did not improve the spectrum. During all manipulations every precaution was taken to prevent moisture from entering the liquids.

CONTRACTION

Precise quantitative measurements of the contraction which occurs when organic matrix solutions are cooled in liquid nitrogen have been reported for a few hydrocarbons, mainly mixtures of iso-pentane and methyl cyclohexane[6]. Average values given elsewhere are said to be valid for several different mixtures[1,3].

A pear-shaped flask (27 ml) was melted on to a 10 ml precision burette equipped with a standard joint. A movable electrical heater, length 5 cm, was wound around the burette and the apparatus was accurately calibrated by weighing. When the hydrocarbon mixture had been poured into the apparatus, the system was out-gassed and closed by means of a stop-cock attached to the burette by means of a standard joint. The volume of the liquid was measured at 293°K in a thermostat and the apparatus was then transferred to a Dewar vessel with liquid nitrogen where it was cooled very slowly. The heater was used to avoid the formation of a deep meniscus in the narrow burette tube. When the volume measurements were made, all portions of the hydrocarbon solutions were in the liquid nitrogen. All mixtures were repeatedly cycled between room temperature and liquid nitrogen, and the measurements were repeated with a second apparatus. The results are given in Table 1.

Table 1. Ratio of specific volume at 77°K and 293°K.
The uncertainties are expressed as mean deviations.

Hydrocarbons	$V_{77^\circ K} / V_{293^\circ K}$
iso-pentane - 3-methyl pentane (6:1)	0.7605 ± 0.0004
iso-pentane - 3-methyl pentane (2:3)	0.7713 ± 0.0004
3-methyl pentane (pure)	0.7845 ± 0.0006
n-pentane - neo-hexane (3:8)	0.7694 ± 0.0005

RELATIVE VISCOSITY

The rigidity of a number of hydrocarbon mixtures has been reported in very general terms[1, 3, 7]. Quantitative viscosity comparisons between different mixtures have not been performed as judged from what has been published. A study was therefore undertaken to compare the temperature ranges in which different mixtures start to become fluid. The velocity of fall of a ball-shaped body was taken as a measure of the viscosity.

A cylindrically shaped copper block wound with a heating wire (8 × 5 cm) was placed in the bottom of a Dewar vessel (45 × 5.6 cm); it was thermally insulated from the inner wall of the Dewar by means of thin cork rings. Two holes, both 6 cm deep, were drilled in the block, one centrally, diameter 1.7 cm, the second, diameter 0.6 cm, close to the first one. A small third hole near the edge of the block carried a glass tube from the outside of the Dewar to its bottom. A cylindrical glass vessel (diam. 1.6 cm) provided with a 40 cm long stem (diam. 0.8 cm) could be inserted in the central hole, and a brass ring fastened to the stem served as a lid for the central cavity. Inside the stem a thin rod (35 × 0.3 cm) made from balsa wood could be moved up and down; it was guided by two small rings of steel placed 25 cm apart on the rod. The lower end of the rod was provided with a stainless steel ball (diam. 0.632 cm), the total weight of the movable part being 2.85 g. The temperature inside the copper block could be measured by means of a platinum resistance thermometer (Type Hereaus BS5) placed in the 0.6 cm hole. The dimensions of the coil were 1.2 × 0.5 cm and its resistance at 273°K was 100 ohms. The thermometer was used in connection with a Mueller G 1 bridge (Type Rubicon 1551), and it was calibrated in liquid oxygen, solid carbon dioxide, ice-water and steam.

The hydrocarbon mixture was poured into the glass vessel until it nearly reached the stem. The falling body was inserted and kept in the upper part of the stem by means of a small magnet outside the tube. The liquid was outgassed and the vessel was closed with a stop-cock attached to the stem by means of a standard joint. Liquid nitrogen was poured into the Dewar until the copper block was surrounded with the liquid, while the glass tube with the hydrocarbons was slowly pre-cooled in another Dewar. Great care was taken to prevent the surface of the glassy mixture from forming a deep meniscus. The hydrocarbon mixture was placed in the copper block and allowed to reach liquid nitrogen temperature. The nitrogen was sucked off and the magnet was removed so that the stainless steel ball rested on the hard upper surface of the glass. When the heater was turned on, 1 watt produced a temperature increase of 0.2° per min. The position of the upper end of the balsa rod was measured and, together with the temperature, plotted against time. When the glass softened, the balsa rod started to move at a rate that was directly found from the plotted curve. Obviously, the slope of the curve represents the velocity of fall. Temperatures corresponding to slopes of 10°, 15°, 20° and 25° were evaluated. At least three independent runs were made for each hydrocarbon mixture. The surprisingly good reproducibility is shown in Figure 1, in which the temperature is plotted against the velocity of fall for a number of hydrocarbons.

The vertical extent of the markings represents the maximum deviation between various runs. A few experiments where the temperature rise was 1° per min. gave exactly the same result.

According to Stokes Law the viscosity is a linear function of the velocity of fall. Although in this case the contact surface between the falling body and the substance is not constant during a run, the experiment can be used to arrange the hydrocarbon glasses in order of increasing rigidity (Figure 1). It is of interest to note that the glasses numbered 5 and 6 are of higher viscosity than 3-methyl pentane. Both are mixtures of methyl cyclohexane and 3-methyl pentane, 2:1 and 6:1, respectively, and have not been used previously. However, they tend to crack when stored for several hours at 77°K, which somewhat limits their use.

MELTING CURVES

If the spectral behaviour of a matrix containing trapped unstable species is to be studied as a function of temperature, it is of importance that the specific heat in the melting region does not show any abrupt change. Therefore, the mixtures previously described were studied in a simple specific heat calorimeter.

A cylindrical glass vessel, diam. 3 cm, of 45 ml volume was equipped with an interior heater consisting of a manganin wire wound on a piece of glass tubing, that had been concentrically sealed into the vessel. The vessel was provided with a long stem through which a Heraeus BS5 platinum resistance thermometer could be inserted. The stem was equipped with five circular, highly polished, thin copper discs, equally spaced, serving as heat shields. The vessel fitted into a long, narrow glass Dewar.

The glass vessel was filled with the hydrocarbon mixture, the thermometer was inserted and the apparatus was outgassed and closed. The hydrocarbon mixture was cooled to 77°K in the Dewar and when this temperature was reached, the liquid nitrogen was removed. The system was then allowed to attain thermal equilibrium, a steady increase in temperature of about 0.1° per min. was reached within 15 minutes. When 0.5 watt was supplied through the heater, the temperature increased at a rate of about 1° per minute (Figure 2). Although the resistance of the heating wire changed, the power was supplied at a constant rate by means of a circuit

described elsewhere[8]. 3-Methyl pentane (pure) and iso-pentane - 3-methyl pentane (6:1 and 2:3) showed an evenly increasing specific heat according to Curve 2. Curve 1 represents a typical run with n-pentane - neo-hexane (3:8). At about 100°K crystallization started and the crystals melted at 121.9 - 122.2°K. Beyond 122°, the curve was found to be a direct extension of the curve below 100°K. The same eutecticum was found with varying composition of the glass and it represents neither of the pure components (n-pentane m.p. 141.7, neo-hexane m.p. 175.0°K). The practical use of the mixture as a matrix is by no means disturbed by the crystallization, which starts at a temperature well above the melting region. Furthermore, crystallization has never been observed during freezing.

The very smooth curves obtained for the iso-pentane - 3-methyl pentane glasses studied conclusively prove the absence of a microcrystalline structure, which might undergo phase transformation below 150°K.

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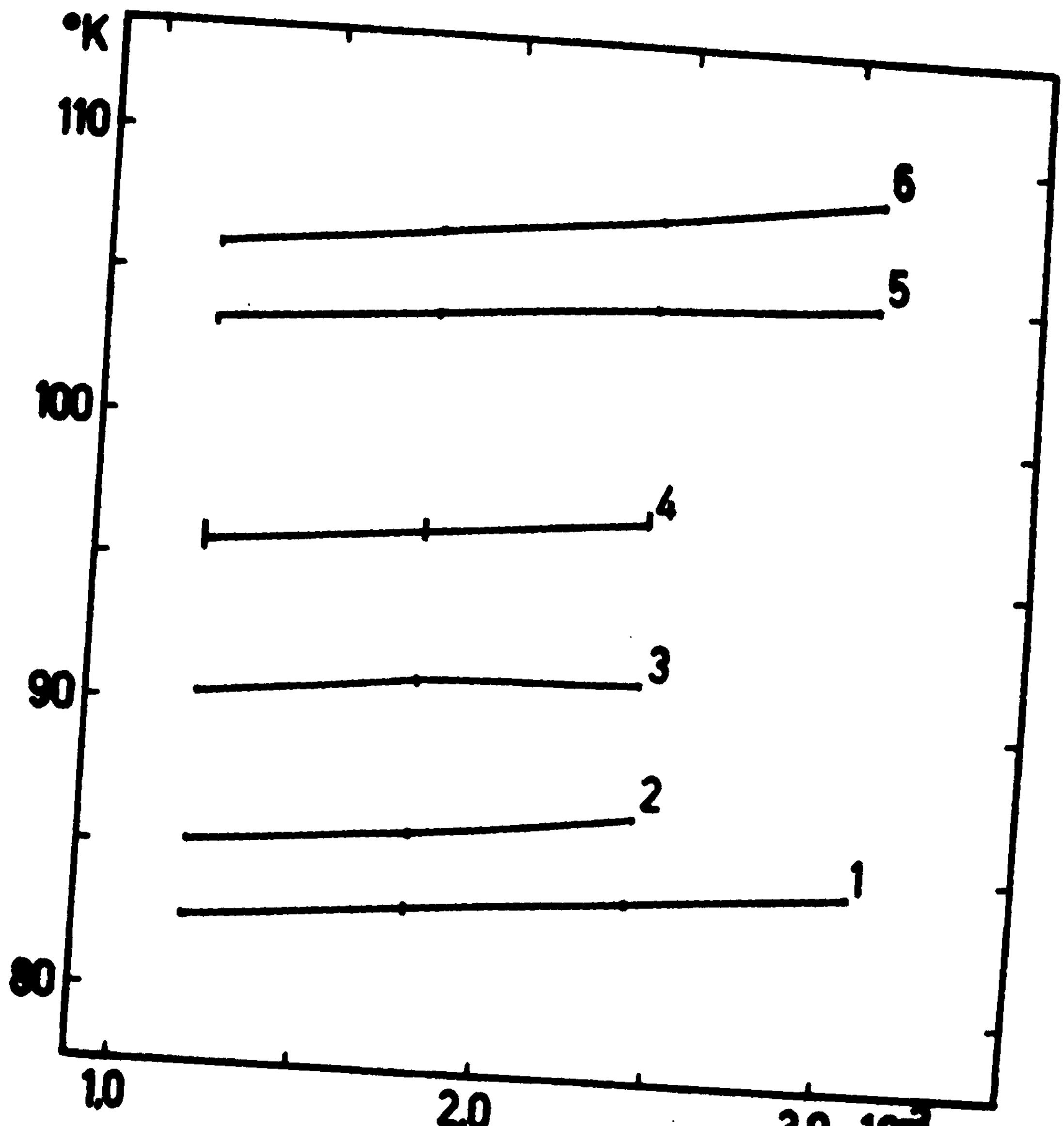
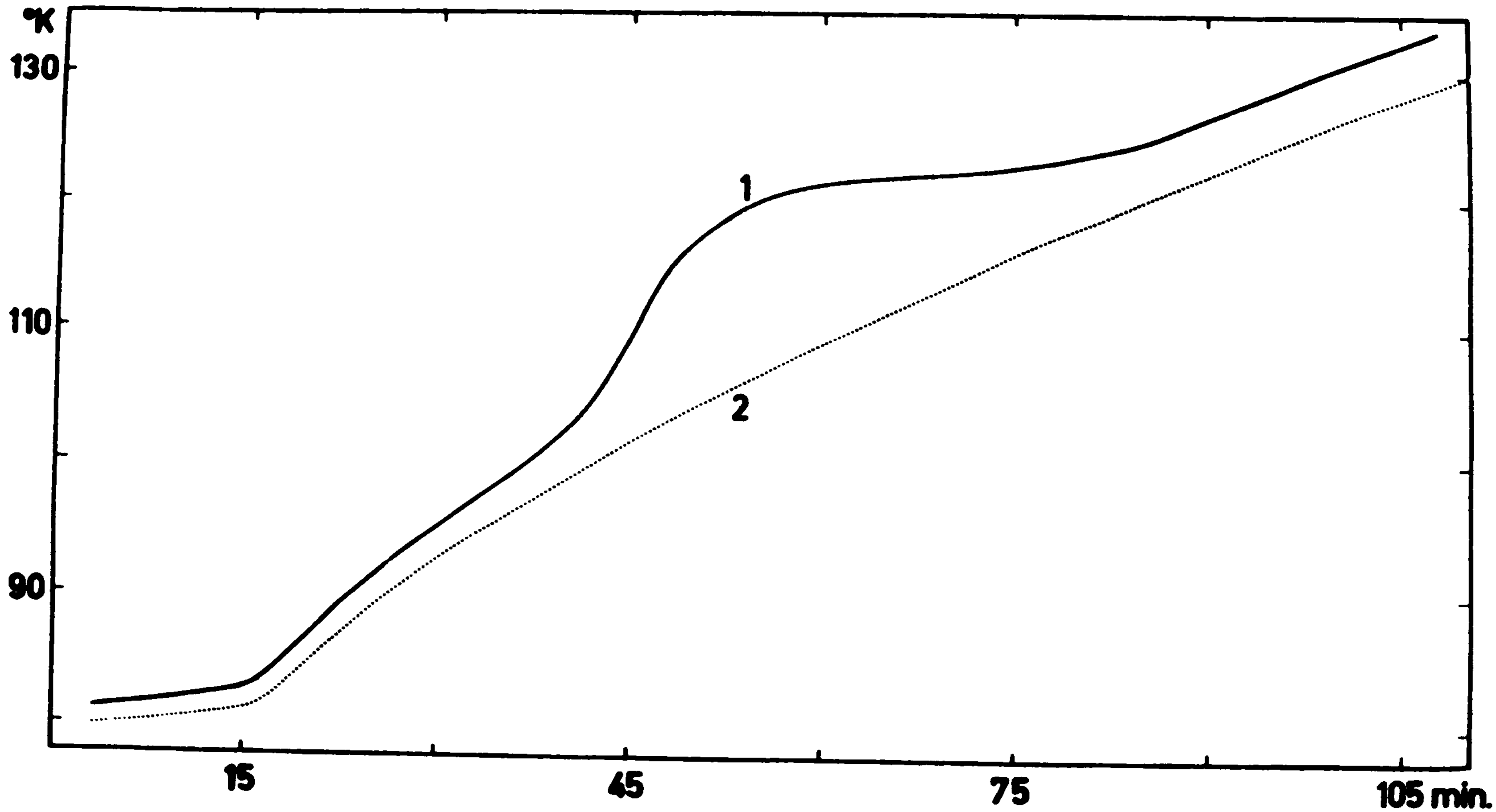


Fig. 1. Relative viscosity for different matrices. (1) i-pentane – 3 methyl pentane 6:1, (2) n-pentane – neo-hexane 3:8, (3) i-pentane – 3 methyl pentane 2:3, (4) pure 3 methyl pentane, (5) 3 methyl pentane – methyl cyclohexane 1:2 and (6) 3 methyl pentane – methyl cyclohexane 1:6.



<u>Fig. 2</u>. Melting curves for (1) <u>n</u>-pentane — <u>neo</u>-hexane 3:8 and (2) <u>iso</u>-pentane — 3 methyl pentane 6:1.

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TECHNICAL NOTE

SOME NEW GLASS-FORMING HYDROCARBON MIXTURES

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ABSTRACT: Binary and ternary mixtures of hydrocarbons have been tested on their ability to form transparent glasses at liquid nitrogen temperature. 3 parts of n-pentane and 8 parts of neo-hexane gave a stable glass, considered to be more inert towards radical attack than previously known glass-forming mixtures, which all contain hydrocarbons with tertiary carbon atoms.

In order to study in detail the photolysis reaction mechanisms in a high-viscosity matrix at 77°K it is necessary to devise conditions and means by which reaction between the photolytically active molecules and the surrounding matrix molecules can be prevented or elucidated. The hitherto used glasses[1-4] based on hydrocarbons consist of one or two of the compounds i-pentane, 3-methyl pentane and methyl cyclohexane, all containing hydrogen attached to tertiary carbon atoms.

On of the predictable reactions between primary photolysis products and matrix molecules is the hydrogen abstraction from a hydrocarbon by a species of radical nature[5,6]. As the C_{tert} - H bond dissociation energy is about 5 kcal less than that for a $C_{sec.}$ - H bond (89 and 94 kcal, respectively)[7], it should be advantageous to have available a matrix without tertiary carbon atoms in the hydrocarbon components. According to the Arrhenius equation, an increase in activation energy of 5 kcal at 77°K changes the rate constant by a factor of 10^{-14}, provided the preexponential factor does not change. Hydrogen bonded to a tertiary carbon atom reacts instantaneously whereas hydrogen bonded to a secondary carbon atom does not react at all.

The following hydrocarbons were purified according to standard procedure[8]: n-pentane (a), i-pentane (b), n-hexane (c), cyclo-hexane (d), 3-methyl pentane (e), neo-hexane (f), methyl cyclo-pentane (g) and methyl cyclo-hexane (h). Binary and ternary mixtures were made and repeatedly cycled between room temperature and 77°K to study their glass-forming properties. The tendency for cracking at 77°K was tested by filling sample tubes with small pieces of broken glass.

The following results were obtained. First, the components of the mixture are given and, secondly, the approximate volume ratio between them, for which a glass with given quality was obtained (in three cases a rather broad ratio interval is given for which glasses have been obtained).

Mixtures forming good glasses at 77°K: a:f, 3:5 - 3:10; b:e, 0:1 - 1:0.

Mixtures forming good glasses, which may crack when stored for hours at 77°K: a:c:f, 1:1:9; a:d:f, 5:2:13; b:e:h, 1:1:1; b:h, 3:2; d:f, 1:9; e:h, 1:2 - 1:6.

Mixtures that crystallized in all proportions during freezing: c:f, e:g, f:g g:h.

Of the mixtures studied, a:f, a:c:f, a:d:f and d:f do not contain tertiary carbon atoms. However, the only one which has been found to give a very stable glass is n-pentane and neo-hexane. In the proportions 3:8, this glass has been extensively used in our laboratory.

Contraction between 298 and 77°K, relative viscosity and melting behaviour for some of these glasses have been studied in the preceding paper[8].

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TECHNICAL NOTE

A SYSTEMATIC STUDY OF THE PHOTOLYSIS OF SOME DIALKYL DISULFIDES IN A RIGID GLASS AT 77°K

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15 January 1962

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ABSTRACT: A number of primary, secondary and tertiary aliphatic disulfides have been photolyzed in a hydrocarbon matrix at $77^{\circ}K$ using super high-pressure mercury lamps together with appropriate filter. The spectral changes have been recorded and the reaction products, obtained after warm-up, have been identified using GLC.

All primary and secondary disulfides (except Me_2S_2) behave in an analogous stoichiometrically simple way (in contrast to tert. butyldisulfide). Strong evidence is presented for the view that the only detectable overall reaction occurring during photolysis is $R_1R_2CHSSCHR_1R_2 \longrightarrow R_1R_2C{=}S + HSCHR_1R_2$. The presence of both reaction products has been established.

The spectral changes during the photolysis of dimethyl disulfide are only initially analogous to those of the other primary disulfides. Upon prolonged irradiation unknown reactions occur, leading to the formation of carbonmonosulfide, CS, among other products.

INTRODUCTION

An experimental study of the possibilities of determining bond-formation energies by direct measurement of the enthalpy change accompanying the radical recombination process

$$2R\cdot \longrightarrow R_2$$

must of course start with the elucidation of the conditions under which one specified, known radical can be produced, quantitatively determined and stored for a sufficiently long period of time. Thus, it is obvious that one should first investigate the homolytic splitting of symmetrical compounds, R - R.

In this field the general lack of knowledge, particularly regarding the stoichiometry of radical formation processes, is such that no guidance can be obtained from the literature in selecting the class of compounds to be studied. However, it has been stated repeatedly in the literature that disulfides upon irradiation can be split into intermediate thiyl radicals: $R_2S_2 \longrightarrow 2RS\cdot$.

In recent reviews Bateman, Moore and Porter[1] and Parker and Kharasch[2] have summarized the experimental indications for the homolytic splitting of the S - S bond under different conditions and they conclude that convincing evidence exists for the homolysis of this bond in photochemical reactions, whereas purely thermal homolysis of the S - S bond in organic di- and poly-sulfide molecules at temperatures below 140°C has not yet been conclusively demonstrated. Lewis and Lipkin[3], when illuminating diphenyl disulfide in a rigid matrix at liquid-air temperature, produced a yellow color that disappeared when the sample was brought to room temperature. This color was believed to be due to the free radical $C_6H_5S\cdot$. Barltrop, Hayes and Calvin[4] photolyzed trimethylene disulfide at 77°K in an EPA matrix. Upon photolysis the cell content became pale salmon-colored and the original disulfide peak at 330 mμ disappeared almost completely. When the temperature of sample was raised a few degrees above liquid nitrogen temperature, the glass lost its rigidity and the cell content rapidly became turbid owing to the formation of polymers. More than 50 % of the original disulfide was recovered. The result from the photolysis was believed to be a diradical $\cdot S(CH_2)_3S\cdot$ which partly polymerized upon warming up. The results of experiments with six simple symmetrical alkyl- and aryl disulfides, aiming at the trapping of free radicals produced under pyrolytic as well as photolytic conditions, have been published by

Michaelson[5]. Among the disulfides sublimed onto a cold finger in vacuo and photolyzed in situ only the aryl disulfides gave a red deposit, which was thought to be due to free radicals formed through homolysis of the S - S bond. When the disulfides were pyrolyzed in vapor phase by allowing them to pass through a furnace kept above 350°C, a colored deposit collected on the cold finger. This deposit was believed to contain radicals, partly of the type RSS· (yellow deposit) and partly of the type RS· (red deposit); the alkyl disulfides gave a deposit predominantly of the former type.

It seemed therefore reasonable to assume that the photolysis of simple disulfides under conditions favorable for the stabilization of intermediate products formed might lead to the isolation and characterization of thiyl radicals.

The technique chosen, Ref.9, was to photolyse the disulfide in a rigid organic matrix at 77°K and to study, primarily, the changes of the UV- and visible spectra. This technique, which has been well established mainly through the work of Norman and Porter[6] and Porter and Strachan[7,8], was early used by Lewis and Lipkin for studying the photolysis of diphenyl disulfide[3]. The present study, however, is only concerned with investigations of aliphatic disulfides. The spectra of these compounds are much less complicated and, moreover, the analysis of possible primary and secondary reaction products is easier to perform.

EXPERIMENTAL TECHNIQUE

Photolysis. The photolysis set-up, consisting of two super high-pressure mercury lamps (900 W each), 35 mm cells filled with nickel sulphate solution (285 g $NiSO_4$, $6H_2O$ per liter) and exchangeable glass filters, has been described elsewhere[9]. In the present investigation Jena filters (WG7 and UG5) have been used. Figure 1 shows the light transmission for the solution proper and the filters.

Spectrophotometry. The cell compartment accomodating two 17×19 mm quartz cells used both for photolysis and spectrophotometry (Unicam recording spectrophotometer SP 700) has been described elsewhere[10].

Experimental procedure. All solutions were prepared and transferred under rigorously anhydrous conditions as even traces of water interfered, particularly in the short wave-length region[11]. The filling and handling of the quartz cells as well as the general procedure for the photolysis and the spectrophotometer has been described elsewhere[9]. All concentrations given in this paper are referred to room temperature. The actual concentration at 77^{o}K is greater by a factor of 1.32 for solutions in matrix "A" and 1.30 for solutions in matrix "B" (see below). The values of molar extinction given have all been corrected for this change in concentration.

Gas-liquid chromatography (GLC) was used to search for reaction products after photolysis. In these experiments disulfide solutions were irradiated in 0.5 mm sealed, clear quartz capillary tubes kept at 77^{o}K in a quartz Dewar vessel equipped with an appropriate heating device to prevent condensation on the outer surface. After photolysis the quarts tubes were opened at 15^{o} (to avoid evaporation of solvents) and 1 µl samples were withdrawn using a fine glass capillary pipette and transferred to a Pye Argon Chromatograph equipped with an ionization detector. The chromatograph had been rebuilt to accomodate columns of 7 mm inner diam. and 120 cm length, either one or three in series.

MATERIALS

Dimethyl disulfide (British Drug House, b.p. 108.5^{o}/760 mm),
diethyl disulfide (Eastman chemicals, b.p. 89^{o}/120 mm),
di-n-propyl disulfide (Eastman chemicals, b.p. 89^{o}/22 mm),
di-i-propyl disulfide (Eastman chemicals, b.p. 72^{o}/20 mm),
di-n-butyl disulfide (Eastman chemicals, b.p. 101^{o}/10 mm),
di-i-butyl disulfide (Eastman chemicals, b.p. 85^{o}/10-11 mm),
di-t-butyl disulfide (Phillips Petr. Co., b.p. 67.5^{o}/9 mm) and
1-butanethiol (British Drug House, b.p. 98^{o}/760 mm)

were all purified by two successive fractional distillations through a glass column, 50 × 1.2 cm, packed with Fenske helices, 4 mm in diam., main fractions being collected at given b.p.'s and pressures. The samples of the compounds used in the experiments showed no impurities when analyzed with GLC except for di-n-propyl disulfide, which contained less than 0.1 % of an unknown substance.

Di-n-decyl disulfide was prepared from fractionally distilled, pure 1-decanethiol by oxidation with iodine. Owing to decomposition, the disulfide obtained could not be further purified by fractional distillation even at low pressures. It was therefore dissolved in absolute ethanol and slowly frozen out on a cold finger using dry ice as a refrigerant. The procedure was repeated twice.

Di-sec-butyl disulfide. A sample of pure 2-butanethiol, prepared from the corresponding bromide and thiourea, [Ref. 12 p. 497], was oxidized with iodine. After two successive fractional distillations at 91°/10 mm a faintly yellow product was obtained, which showed less than 0.1 % impurities (GLC).

Di-cyclohexyl disulfide. Pure cyclohexanethiol, prepared from the corresponding bromide and thiourea, was oxidized with iodine. The disulfide was fractionally distilled twice at 98°/2 mm. The colorless main fraction showed less than 0.5 % impurities (GLC).

Di-neopentyl disulfide. Neopentylmercaptan prepared from neopentyl alcohol and p-toluene sulfonylchloride[13] was oxidized with iodine. The disulfide was purified by twofold fractional sublimation in vacuum and was recovered as a white solid, m.p. 40-41°C. GLC showed less than 0.1 % impurities.

Cyclohexanethione was prepared from cyclohexanone according to Sen[14]. The substance was fractionally distilled in vacuum into five receiver flasks which were cooled one by one with liquid nitrogen during the distillation and sealed off as soon as a sufficient quantity had been collected. The deep-red colored fraction, boiling at 66°/16 mm, was used for the experiments.

2,4,6-trimethyl trithiane (α and β) were prepared from thioacetaldehyde, HCl and H_2S[15]. M.p. 101°C and 125-126°C, respectively.

Solvents. All hydrocarbons used, i-pentane (techn. grade), n-pentane (pure grade), neo-hexane (pure grade) and 3-methyl pentane (techn. grade), were supplied by Phillips Petroleum Company. They were carefully purified by fractional distillation followed by adsorption on silica gel, the details have been described elsewhere[16].

The matrix forming hydrocarbon mixtures used in this work were:

$$\left.\begin{array}{l}\text{iso-pentane (6 parts)}\\ \text{3-methyl pentane (1 part)}\end{array}\right\}\quad \text{called matrix "A"}$$

$$\left.\begin{array}{l}\text{neo-hexane (8 parts)}\\ \text{n-pentane (3 parts)}\end{array}\right\}\quad \text{called matrix "B"}$$

Some properties of these mixtures will be given elsewhere[16, 17].

EXPERIMENTAL RESULTS

Preliminary experiments

In order to see if an extremely low quantum yield at 77°K could make the photolysis of the disulfide molecule impossible, a 20 mM solution of Et_2S_2 in matrix "B" was photolyzed in quartz capillary tubes both at room temperature and at 77°K. Besides the disulfide, the hydrocarbon mixture contained 0.1 % n-octane as a reference substance for the gas chromatographic analysis. After photolysis and warm-up, five identical samples were withdrawn from each tube and run through the gas chromatograph. The ratio $\frac{\text{area under } Et_2S_2 \text{ peak}}{\text{area under n-octane peak}}$ was taken as a measure of the disulfide concentration. The results are given in Table 1 which shows that the quantum yield is of the same order of magnitude at the two different temperatures.

Table 1. Photolysis of 20 mM Et_2S_2 in matrix "B", 0.1 % n-octane added. WG7 filters.

Time of photolysis	Remaining Et_2S_2 % at 298°K	Mean value	Remaining Et_2S_2 % at 77°K	Mean value
10 min.	80.5		84.4	
	82.5	81.5	80.5	82.5
20 min.	76.0		64.3	
	74.6	75.3	64.7	64.5
40 min.	62.0		42.4	
	62.7	62.4	47.0	44.7

A plot of log (% remaining Et_2S_2) against the time of photolysis (Figure 2) indicates the expected first order decay at 77°K, whereas at room temperature the rate constant of the reaction seems to decrease for prolonged photolysis, probably as a result of the formation of light absorbing secondary reaction products which reduce the amount of active light.

When photolyzed under the same conditions methyl disulfide decomposed at about the same ratio as Et_2S_2. However, for 77°K the decay did not fit a first order plot.

When a mixture of methyl- and ethyldisulfides was exposed to UV-light, the mixed disulfide was formed. The equilibrium for this mixture has recently been studied[18]. To check if this also occurs in a rigid environment, a solution containing 20 mM Et_2S_2, 20 mM Me_2S_2 and 0.1 % n-octane in matrix "B" was photolyzed in quartz capillary tubes both at 77°K and at room temperature. The results from the gas-chromatographic analyses are shown in Table 2, which gives the ratio of "area under disulfide peak"/"area under n-octane peak". In addition the equilibrium constant $\frac{MeSSEt^2}{Me_2S_2\ Et_2S_2}$ is given for the photolysis at room temperature, this constant being corrected for the different response of the detector for various disulfides[x].

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[x] This correction is taken from Ref. 18 as the same detector was used in both experiments.

Table 2. Photolysis of 20 mM Me_2S_2 and 20 mM Et_2S_2 in matrix "B", 0.1 % n-o :tane added. WG7 filters.

Time of photolysis	Me_2S_2/n-octane	MeSSEt/n-octane	Et_2S_2/n-octane	K
20 min. at room temp.	2.26	4.60	1.97	4.7
	1.81	3.94	1.74	4.9
	1.47	3.88	1.79	5.6
			Mean value	5.1
40 min. at room temp.	1.67	3.39	1.42	4.8
	1.95	3.93	1.53	5.1
	1.34	3.49	1.60	5.6
			Mean value	5.2
2 min. at 77°K	2.62	0.14	3.45	
5 min. -"-	2.59	0.17	3.42	
10 min. -"-	2.13	0.19	3.16	
20 min. -"-	1.90	0.25	2.94	
30 min. -"-	1.67	0.22	2.45	
40 min. -"-	1.31	0.22	1.98	
Blank, unphotolyzed	2.86	0.10	3.63	
	2.80	0.16	3.58	

As is seen from Table 2 the mixed disulfide is formed very rapidly at room temperature and the value of K is already after 20 minutes of photolysis very close to the equilibrium constant previously reported (average 5.6). At 77°K, however, no significant correlation can be found between the amount of mixed disulfide formed and the time of photolysis. The small amount of mixed disulfide found at 77°K is probably formed during the manipulation of the quartz capillary tubes. The reaction may, for instance, be caused by the ultraviolet light produced when the tubes are melted off in a hydrogen flame. It is of interest to notice that most spectrophotometric experiments have been performed in ca. 400 times more dilute solutions, in which the average distance between neighbouring disulfide molecules is increased by a factor of 7 (Cf. below).

From the preliminary experiments it was apparent that, to a considerable extent, disulfide disappears irreversibly during photolysis followed by warm-up. At 77°K the decomposition reaction was found to be, within the limits of error, unimolecular, indicating a direct dependance on the excitational process. Further, the

experiments with mixtures of disulfides show that, whatever the reaction mechanism is, an excited disulfide molecule cannot diffuse in the solid matrix to be able to react with a second disulfide molecule.

Although, the preliminary results, concerning the possibility of utilizing the chosen method for thermochemical studies of radical recombination energies, were discouraging, it was felt necessary to gain further knowledge of the causes for the apparent failure. Only in this way can one devise experimental conditions, whereby the original idea could be successfully realized.

Spectrophotometric results.

Prim-alkyl-disulfides. A cell containing 0.4 mM n-butyl disulfide in matrix "A" together with an appropriate reference cell were cooled down to 77°K inside the cell compartment previously described. An ultraviolet spectrum was recorded after which the solution was photolyzed for a few minutes using WG7 filters. When a new spectrum was recorded shortly after the end of the photolysis period the disulfide peak at 40 kc. cm^{-1} had decreased (Figure 3). Repeated recordings of the spectrum at various times showed no change in transmission after the end of the photolysis as long as the liquid nitrogen level was kept above the optical path. Repeated photolysis resulted in a further decrease of the disulfide peak and if the spectra after various times of photolysis were recorded on the same paper an isosbestic point at 40.85 k c. cm^{-1} showed up.

The various curves were analyzed and log (% remaining disulfide) at different wavenumbers was plotted against the time of photolysis. A strict first order decay was found in a small wavenumber region for photolysis times less than ca. 30 min. Figure 4 shows the results from a typical run; the vertical extent of the four marks represents the maximum deviation when the disulfide concentration is measured at four equally spaced wavenumbers from 37.6 to 38.8 k c. cm^{-1}. Outside this wavenumber region the calculated values did not fit the straight line indicating the formation of light-absorbing reaction products.

The frozen cells were brought to room temperature and the spectrum recorded as soon as possible. This could usually be started within 3-5 minutes after the disulfide containing cell was lifted up from the liquid nitrogen. Comparison with the spectrum recorded before the cells were frozen down showed that the

amount of remaining disulfide after warm-up was the same as the amount of remaining disulfide measured at 77°K after the last photolysis. The spectrum after warm-up changed slightly with time as shown in Figure 5.

In order to study more carefully the high absorption peak which was developed during photolysis the experiment was repeated using 0.05 mM disulfide. Figure 6 shows the spectra recorded after increasing times of photolysis. As is seen from the Figure a broad band with a maximum at 45.2 kc.cm^{-1} was created. If the reaction product, responsible for this peak, was formed in the first-order decay reaction, its optical density ought to increase at any wavenumber with time of photolysis according to the following equation[x]:

$$D = \varepsilon C_o l(1 - e^{-kt})$$

D = optical density
ε = molar extinction coefficient of the reaction product
C_o = initial concentration of the disulfide
l = cell length
k = rate constant of the reaction
t = time of photolysis

Figure 7 gives the optical density at various wavenumbers plotted against e^{-kt}. The optical density values have all been corrected for remaining unphotolyzed disulfide. A set of different values for k had to be tried until a particular value gave straight lines. In the given experiment k was found to be 0.046 min^{-1}, which corresponded to $t_{1/2}$ = 15 minutes. The straight lines could be extrapolated to infinite time of photolysis ($e^{-kt} = 0$) and thus the molar extinction coefficient for the reaction product at 77°K could be obtained; log ε_{max} = 3.96.

A spectrum recorded a few minutes after the photolyzed solution was brought to room temperature is shown in Figure 8 (curve 3). The high absorption peak was still present, although somewhat lowered and shifted about 0.2 k c. cm^{-1} towards higher wavenumbers. In addition, a more intensive absorption peak became visible at 48.4 k c. cm^{-1}. The appearence of this peak was fully reversibly

x) It is obvious that this equation is valid also if two identical species are formed per disulfide molecule, the calculated molar extinction coefficient in this case being twice the true one.

dependent on the temperature[x]. Curve 4 (Figure 8) shows the spectrum when the optical cells were cooled to 77°K for the second time. The small discrepancy between curves 4 and 2 could be ascribed to dilution of the photolysis product with some unphotolyzed disulfide solution remaining in the stem of the optical cell during photolysis. Repeated cycling of the probe between 77°K and room temperature always gave the same result as far as the appearence of the peak at 48.4 kc.cm^{-1} was concerned.

If the photolyzed solution was allowed to stand at room temperature, a slow decrease in absorption, as shown in Figure 9, could be noticed. It was found that the ratio between the two maxima did not change. Similar experiments repeated with matrix "B" gave identical results, which was also the case when two sets of filters, other than WG7, were used in the light path, viz. WG6 and KG2, high wavenumber cut off at 41.2 and 40.6 kc.cm^{-1}, respectively.

All observations described have been reproduced in a number of runs and, further, experiments with ethyl-, n-propyl-, iso-butyl- and neo-pentyl-disulfides have been performed, all showing the same detailed behaviour with exception of minor differences regarding the spectrophotometric characters of the photolysis product. The results have been summarized in Table 3. n-Decyl disulfide also gave the same results with the exception that the isosbestic point was observed at 39.7 kc.cm^{-1}. The solutions of this disulfide became turbid when frozen down to 77°K, and no accurate kinetic determinations could therefore be made. However, the rate of photolysis seemed to be considerably lower than that of the other primary disulfides. The spectrum of neo-pentyldisulfide did not differ from other primary or secondary alkyldisulfides. At room temperature in matrix "A" the maximum appeared at 39.0 kc.cm^{-1}; log ε_{max} = 2.48.

Secondary alkyl disulfides. The investigated secondary alkyl disulfides (i-propyl-, sec-butyl- and cyclo-hexyl) also gave analogous results (Table 3), although the high absorption peak and the isosbestic point were shifted towards lower wavenumbers, 44.0 and 39.3 kc.cm^{-1}, respectively. The extrapolated log ε_{max} for the photolysis

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[x] This temperature-dependent absorption is at present without explanation - it has been found in all cases studied with two exceptions - dimethyl and dicyclohexyl disulfide. By independent control experiments it has been established that the spectrophotometer is reliable down to 51 kc.cm^{-1}.

Table 3. Spectrophotometric characters at 77°K of the photolysis product for various dialkyl disulfides. Figures in brackets indicate the number of experiments. The uncertainties expressed as mean deviations.

	Wavenumber of peak		Wavenumber of isosbestic point		log ε_{max}	
Me_2S_2	48.07	(1)	43.31±0.04	(4)	(3.8)	(1)
Et_2S_2	45.50±0.05	(5)	41.08±0.03	(6)	3.91±0.03	(3)
n-Pr_2S_2	45.27±0.05	(2)	40.96±0.06	(3)	4.0 ±0.1	(1)
n-Bu_2S_2	45.21±0.03	(7)	40.85±0.04	(10)	3.94±0.03	(6)
i-Bu_2S_2	45.06±0.02	(2)	40.86±0.02	(3)	3.91±0.07	(2)
neo-$Pentyl_2S_2$	44.97±0.02	(2)	40.55±0.04	(2)	4	(2)
i-Pr_2S_2	44.00±0.03	(2)	39.11±0.03	(3)	3.96±0.02	(2)
sec-Bu_2S_2	44.03±0.04	(3)	39.26±0.03	(5)	3.94±0.02	(2)
cyclo-$Hexyl_2S_2$	44.60±0.03	(2)	40.27±0.03	(3)	3.91±0.04	(2)

product at 77°K was also in this case about 4. The secondary disulfides gave somewhat different results after warm-up. For iso-propyl- and sec-butyl-disulfides the two peaks visible at room temperature were moved closer to each other and the reversible one dominated so strongly in intensity that the original peak at 44 $kc.cm^{-1}$ was visible only as a shoulder (Figure 10, curve 3). Cyclo-hexyl disulfide gave no second peak upon warm-up; the maximum appeared at 44.6 $kc.cm^{-1}$ both at 77°K and at room temperature.

Tertiary alkyldisulfides. The spectrum of tert-butyl disulfide does not show the disulfide maximum at 40 $kc.cm^{-1}$ [19]; only a weak shoulder is seen at room temperature with inflections at ca. 40 and 44 $kc.cm^{-1}$ [x]. When a solution in matrix "A" was cooled to 77°K a maximum became visible at 44.6 $kc.cm^{-1}$ (log ε_{max} = 2.97); a minimum appeared at 46.7 $kc.cm^{-1}$ (log ε_{max} = 2.87) and the absorption again increased at higher wavenumbers.

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[x] If log ε is plotted against wave-length, the shoulder almost vanishes. Cf. Ref. 19.

A 0.25 mM solution in matrix "A" was photolyzed at 77^{o}K using UG5 filters. The disulfide maximum decreased during photolysis in the whole range 48 - 35 kc. cm^{-1}, neither the isosbestic point nor the high absorption peak was found. When the disulfide concentration had decreased to about 50 % of its initial value, the absorption again rised slowly and a new maximum appeared at 45.5 kc. cm^{-1}. After one and a half hours of photolysis the initial optical density was restored. The complicated kinetic pattern prevented a straight-forward analysis. The 45.5 kc. cm^{-1} peak disappeared during warm-up, and the spectrum at room temperature showed only a continuously increasing absorption towards higher wavenumbers. After a second cooling to 77^{o}K the peak became visible again.

<u>Methyl disulfide</u> gave, when photolyzed at 77^{o}K in a 0.05 mM solution in matrix "A" with WG7 filters, a high absorption peak at 48.1 kc. cm^{-1}, an isosbestic point at 43.3 kc. cm^{-1} and an extrapolated value of log ε_{max} = 3.8, the last value is somewhat uncertain as the high wavenumber region made a precise measurement difficult. The spectrum at room temperature of the photolysis product is shown in Figure 10 (curve 1). The absorption decreased when the sample was allowed to stand at room temperature.

Figure 11 shows results obtained with a 0.5 mM solution under otherwise identical conditions. The total time of photolysis in minutes is given with each curve. The three first curves all passed through the isosbestic point at 43.3 kc. cm^{-1}, but the curve recorded after 16 minutes showed a beginning additional absorbance at this wavenumber and a peak at 31.9 kc. cm^{-1} became clearly visible. The last two spectra show these characteristics even more pronounced, a further distinctive feature seen here is a double peak with maxima at 38.18 and 39.20 kc. cm^{-1}. At the end of the photolysis the cell content was turbid, and when the sample was brought to room temperature traces of a voluminous colorless precipitate were seen at the bottom of the cell. The spectrum now mainly consisted of one sloping line ranging from 46 to 28 kc. cm^{-1}. An inflection clearly indicated that the broad peak at 31.9 kc. cm^{-1} was still there but that the double peak at 38-39 kc. cm^{-1} had disappeared. It did not become visible again after recooling to 77^{o}K.

<u>Disulfides at high concentrations.</u> Ethyl-, <u>n</u>-butyl- and <u>cyclo</u>-hexyl disulfides have also been photolyzed in 5 mM solutions in matrix "A" at 77^{o}K using WG7 filters. When irradiated for about an hour these solutions all gave a faint absorption in the visible part of the spectrum ranging from 30 to 17 kc. cm^{-1}. A weak maximum was found around 20 kc. cm^{-1}. The sample cell when lifted up and viewed perpendi-

cularly to the light path showed two thin dark yellow layers close to the two parallel windows. The rest of the cell had a pale rose color which persisted when the sample was brought to room temperature whereas the yellow color disappeared when the cell content lost its rigidity. A spectrum recorded at room temperature showed an absorption between 23 and 17 kc. cm^{-1} with a maximum at 19.5 kc. cm^{-1}. However, the reduction in transmission never exceeded 10 % even at peak maximum.

The yellow color was probably due to the photolysis of mercaptan formed from the disulfide[20]. Several filter combinations were tried, without positive result, in order to achieve a light induced splitting of the disulfide without simultanous photolysis of the mercaptan.

Mercaptans. Alkyl mercaptans when photolyzed at low concentrations (0.05 and 0.4 mM) in matrix "A" at 77°K using WG7 filters showed very small changes in the spectrum after as much as an hour of irradiation, the most characteristic sign being an increased transmission around 48 kc. cm^{-1}. Besides, the transmission was reduced by a few percent at the mercaptan peak for the most concentrated solution.

Cyclohexanethione. The spectrum of cyclohexanethione has been investigated by Sen[21] and by Janssen[22]. Janssen found in cyclohexane a broad band ranging from 25 to 17 kc. cm^{-1} with a maximum at 19.8 kc. cm^{-1}. He also found a rather high ultraviolet absorption owing to impurities but concluded that "cyclohexanethione has no strong absorption band (log $\varepsilon > 3.5$) at wavelengths above 220 mμ". Owing to the high rate of equilibration between the thione- and its corresponding enethiol-form, 1-cyclohexenethiol, the recorded spectrum cannot, however, be very reliable in the UV-region[14].

A 0.1 mM solution in matrix "A" was prepared and the recording of a spectrum started within 30 minutes after the sealed-off flask containing cyclohexanethione was brought to room temperature (see under MATERIALS). The spectrum at 25°C consisted of a rather broad band starting at 35 kc. cm^{-1} with one maximum at 43.6 kc. cm^{-1} and an inflection unveiling a second somewhat lower maximum at about 46.3 kc. cm^{-1}. At 77°K only one peak was seen at 44.3 kc. cm^{-1} (log ε_{max} = 3.74, assuming the substance to be pure thione-form); no trace of the second peak was visible. The 19.8 kc. cm^{-1} absorption maximum could be verified only at high concentrations (calculated total concentration 20 mM, 85 % transmission).

2, 4, 6-trimethyl-trithiane. The spectrum of sym -trithiane was taken in ethanol and in matrix "A" at room temperature, and the results verified earlier measurements; with an absorption peak at 41.7 kc. cm^{-1} (log ε_{max} = 3.16)[23]. α - and β-2, 4, 6-trimethyl-trithiane were studied in 0.2 mM solutions in matrix "A". Both spectra looked very similar to that of sym-trithiane (peak at 41.9 kc. cm^{-1}, log ε_{max} = 2.94).

Control experiments. Pure samples of the hydrocarbon solutions used were photolyzed at 77°K. When WG7 filters were used, half an hour of irradiation did not change the 100 % - line. If the glass filters were removed a further hour of photolysis caused a small change (about 10 %) around 48 kc. cm^{-1}, where the transmission increased.

Photolysis of n-butyl disulfide at room temperature was carried out in a 0.05 mM solution in matrix "A". The absorption peak at 45.2 kc. cm^{-1}, found at low temperature, could be easily seen, although the spectrum was very obscure. However, the intensity was reduced by a factor of ten.

Gas chromatographic results.

n-Butyl disulfide was photolyzed in quartz capillary tubes and analyzed for 1-butanethiol by means of the gas chromatograph. All experiments were carried out at 77°K using WG7 filters. After irradiation the tubes were kept in liquid nitrogen until they were opened for analysis. From each tube at least five identical samples were withdrawn and put on the column. The mercaptan could be quantitatively estimated by comparison with n-octane as reference substance. Measurements were made using initial disulfide concentrations of 10 and 20 mM in matrix "A". The time of photolysis varied from 10 to 60 minutes. Mercaptan was found in all photolyzed samples, the amount varied with the time of photolysis and in some of the tubes irradiated for one hour it corresponded to a 60 % conversion of the initial disulfide assuming a 1 to 1 ratio. Attempts were made to increase the yield. It seemed, however as if ca. 60 % represented an upper limit. Unphotolyzed blanks showed no trace of mercaptan.

DISCUSSION

Even the preliminary experiments have made clear three important points for the elucidation of the chemical reactions occurring after irradiation of disulfides: First, it was found that the disulfide irreversibly disappeared in the reaction; secondly, the decomposition was found to be a first-order reaction. Thirdly, it was shown that diffusion of disulfide molecules or alkyl thiyl radicals must be completely or nearly completely hindered in the matrix at 77°K.

The spectrophotometric investigationsin all cases fully confirmed the occurence of irreversible chemical reactions upon photolysis. The very regular change in spectral pattern obtained for primary and secondary disulfides showing a precise isosbestic point at about 40 kc. cm^{-1} strongly indicated a simple and well-defined chemical reaction to proceed during the irradiation. Further, the kinetics corresponded strictly to that of a first-order reaction as shown by the disappearance of disulfide as well as by the formation of a photolysis product. Although every effort was made to detect spectrophotometrically, after irradiation, the presence of some unstable species that might be of a radical nature, no trace of such a species could be found by the method used.

Taking the given facts into consideration it was concluded that the irradiation initiates a chemical reaction which takes place in the nearest environment of the excited disulfide molecule and leads to the formation of stable molecular species.

Turning to the problem of the nature of this reaction, the following facts must be considered. The difference in behaviour between the primary and the secondary disulfides and the <u>tert.</u> butyl disulfide is striking. The spectral change during photolysis of the last compound is complicated and does not allow a simple analysis. The discrepancy can hardly be explained as a result of steric factors, as <u>neo</u>-pentyl disulfide behaved normally. In the literature it has often been postulated that hydrogen abstraction from an atom adjacent to a radical site is very easily achieved. In particular, much evidence has been collected for a disproportionation of alkoxyl radicals according to the reaction[24]:

$$2 R_1R_2CHX\cdot \longrightarrow R_1R_2C{=}X + HXCHR_1R_2$$

where X = O, R_1 = Alk and R_2 = Alk, H.

The same mechanism has been proposed by Coope and Bryce[25] for the thermal degradation of Me_2S_2. These authors found that 1 mole of MeSH was formed per mole of Me_2S_2, together with a product that was assumed to be polymeric thioformaldehyde. It is therefore suggestive that only those disulfides with at least one hydrogen atom in the α -position react in a simple manner as judged from the spectrophotometric evidence. The assumption was therefore made that the analogous reaction, X = S, occurs, following the homolytic splitting of the disulfide to identical thiyl radicals.

In accordance, the experiments showed n-butanethiol to be formed in increasing amounts during continued photolysis of butyl disulfide. The observation that the yield could not be increased above 60 % is in good agreement with the results obtained by Walling and Rabinowitz[26]. These authors studied the photolysis of 0.2 - 0.035 M iso-butyl disulfide in cumene at 35°C and found that the yield of 2-methyl 1-propanethiol reached a constant level after a certain period of photolysis. They concluded that this level corresponded to a steady state in which the thiol was decomposed by the light at the same rate as it was formed.

Direct evidence for the formation of mercaptans even at 77°K is obtained from the photolysis experiments on disulfides at high concentrations. The yellow color formed upon prolonged photolysis, and irregularly distributed in the sample cell, was also found to be a general feature accompanying photolysis of mercaptans under otherwise similar conditions[20]. The subsequent photolysis of mercaptan formed in the primary chemical reaction also explains the fact that, at 0.4 mM concentrations, the kinetics of the reaction did strictly follow a first-order rate equation only until about 60-70 % of the disulfide was decomposed (Figure 4).

Provided the above explanation holds, the second reaction product must be a thio aldehyde or a thioketone, depending on whether the disulfide used is primary or secondary. The ease with which the aliphatic thials and thiones trimerize or polymerize makes it extremely difficult to determine the physical properties of the monomers. The only known compound that could be used for the purpose of spectral comparison was cyclohexanethione which further suffers from the disadvantage that it rapidly isomerizes to cyclohexenethiol. Janssen[22] has pointed out that the visible absorption of the thione monomer gradually disappears at room temperature, whereas the ultraviolet absorption remains constant. As expected, both cyclohexenethiol and the trimerized cyclohexanethione exhibit absorption only in the UV-region.

The absorption spectra recorded for the photolysis products from cyclohexyl disulfide and from the sample of freshly distilled cyclohexanethione both show the same peak at 19.8 kc.cm^{-1}. Even if the aforementioned difficulties made a comparison at higher wavenumbers rather doubtful, it is striking that the high absorption maximum was found at 44.3 kc.cm^{-1} (log ε_{max} = 3.74) for the sample of cyclohexanethione and at 44.6 kc.cm^{-1} (log ε_{max} = 3.91) for the photolysis products. In calculating ε_{max} for the sample of cyclohexanethione it was assumed that the substance was pure. According to Sen[14], a freshly distilled sample of cyclohexanethione holds only 62 % of thione-form, the rest being the enethiol isomer. If this is accounted for, the recalculated ε_{max} - value becomes 3.95. The excellent agreement may be fortuitous but strengthens the almost obvious conclusion that the cyclo hexanethione found during photolysis cannot protomerize in the matrix. The spectrum extrapolated from the kinetic measurements must therefore be due to pure thione-form together with cyclo-hexenethiol. The molar extinction of thiol at 44-45 kc.cm^{-1} is in any case less than 3 % of that of the thione and thus the mercaptan does not interfere significantly with the calculation.

After photolysis of a primary and secondary disulfide it has quite generally been found that, after warm-up, the transmission increases at wavenumbers above about 41 kc.cm^{-1} (Figure 9) and decreases in the range 41-36 kc.cm^{-1} (Figure 5). This change can best be explained by referring to the trimerization of the thial or thione formed during photolysis.[x)] The trimeric ethanethial has a spectrum with a peak at 41.9 kc.cm^{-1}. The spectrum of the monomer, on the other hand, has a broad maximum extending below 38 kc.cm^{-1} with the double-peaks at 45.4 and 48.5 kc.cm^{-1} (room temperature, absorption curve corrected for the presence of ethanethiol and remaining disulfide). If the absorption curves are plotted on the same diagram for a molar ratio of monomer to trimer equal to 3:1, the curves intersect at 40.5 kc.cm^{-1} with an estimated error of less than 0.5 kc.cm^{-1}. Thus, if a set of absorption curves were recorded from time to time during the trimerization reaction, an isosbestic point should be found at the intersection wavenumber. From the experiment a value of 40.5 kc.cm^{-1} was found.

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x) At an early stage of the present investigation the increase in absorption between 41-36 kc.cm^{-1} was taken as an indication of a recombination reaction leading to an increase in the amount of disulfide present in the solution. Cf. Ref. 27.

As a whole the facts are strongly in favour of the suggested reaction. From a mechanistic point of view the most simple explanation[x)] would be that the primary step upon excitation is a symmetrical homolytic splitting of the disulfide molecule into two identical thiyl radicals. The subsequent reaction is governed by the close contact between the fragments. Owing to the cage effect[26], the radicals cannot diffuse into the hydrocarbon matrix and have to react either with each other or with matrix molecules. Apparently the α-hydrogen abstraction is the most favoured reaction.

The photolysis of dimethyl disulfide (Figure 11) initially showed the same characteristics as the other primary disulfides studied, especially at low concentrations. The increase in absorption above 43.3 kc. cm^{-1} with a peak at 48.1 kc. cm^{-1} indicated the formation of monomeric thioformaldehyde. Upon prolonged irradiation, however, presumably secondary photolysis reactions occurred, leading to the formation of several products, one of which could be identified as CS with a double peak at 38.16 and 39.20 kc. cm^{-1}. Carbon monosulfide obtained by photolysis from CS_2 showed the CS double-peaks at 38.16 and 39.20 kc. cm^{-1} under otherwise identical conditions[9]. The reaction mechanism is unknown and further experimental studies must be made before an elucidation can be proposed.

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x) Owing to the presented experimental facts, an intramolecular rearrangement mechanism with a four-numbered ring structure in the transition state can not be excluded.

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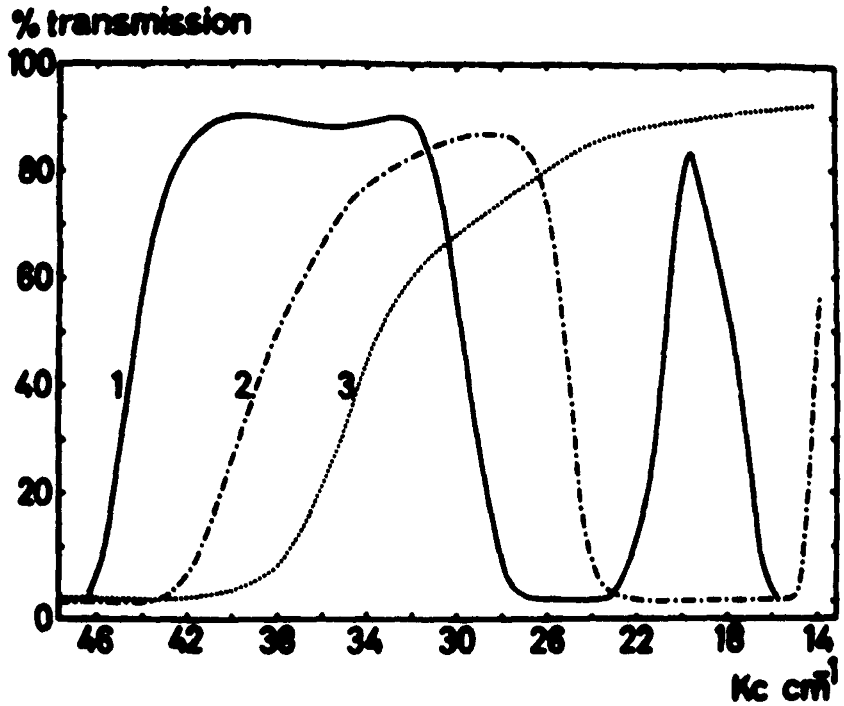


Fig. 1. Light transmission of filters used in the present work. (1) $NiSO_4$, $6H_2O$, 285 g/l, 3.5 cm. (2) Jena filter UG5, high wavenumber cut off 44.3 Kc.cm^{-1}. (3) Jena filter WG7, high wavenumber cut off 43.6 Kc.cm^{-1}.

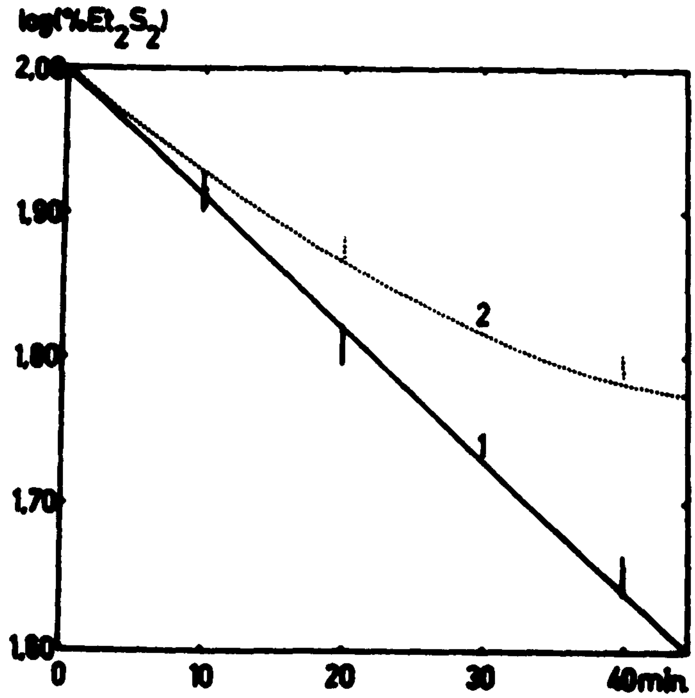


Fig. 2. Log (% remaining ethyl disulfide) from photolysis experiments in matrix "B", plotted against time of irradiation (1) at 77°K, (2) at 298°K.

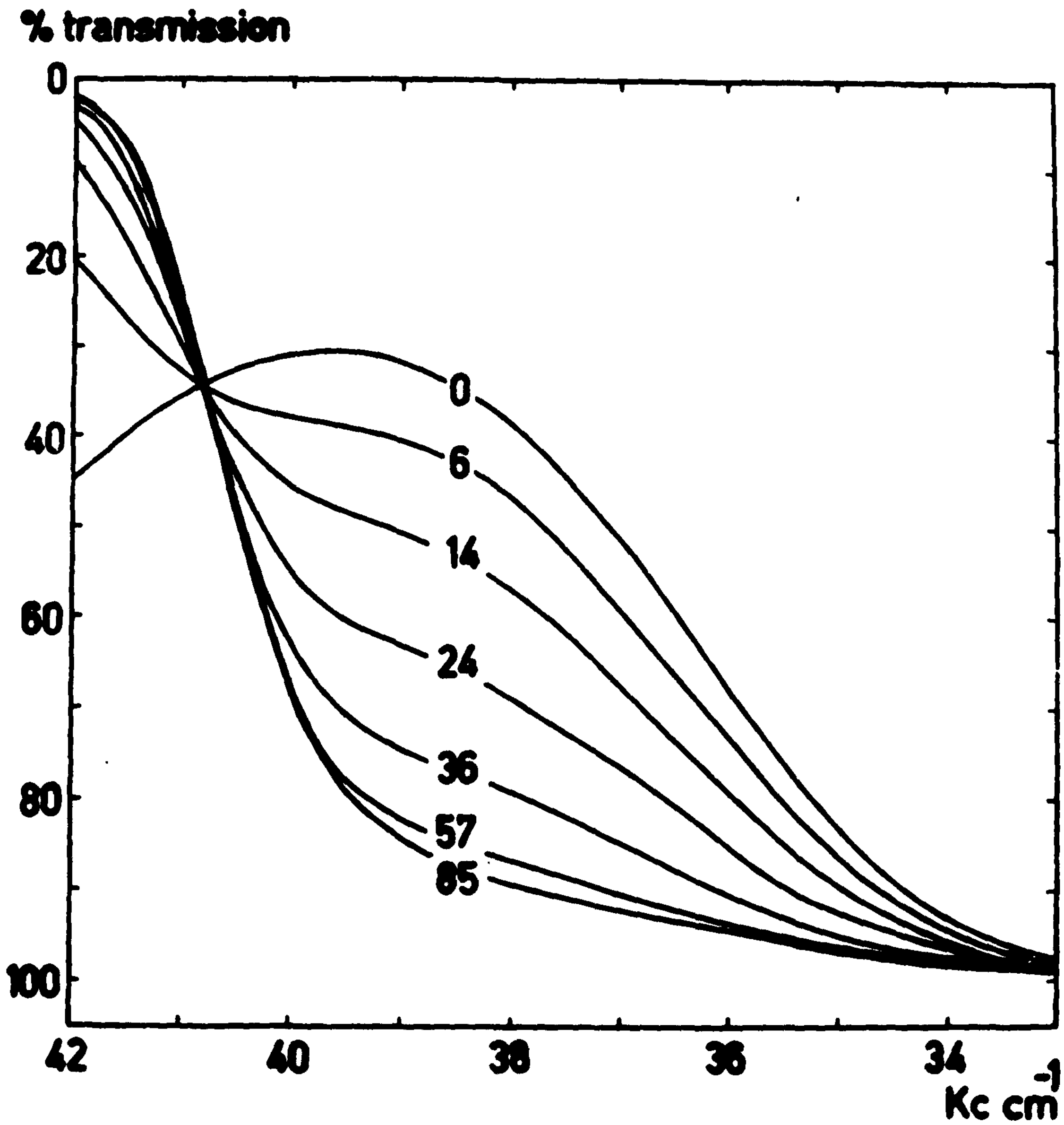
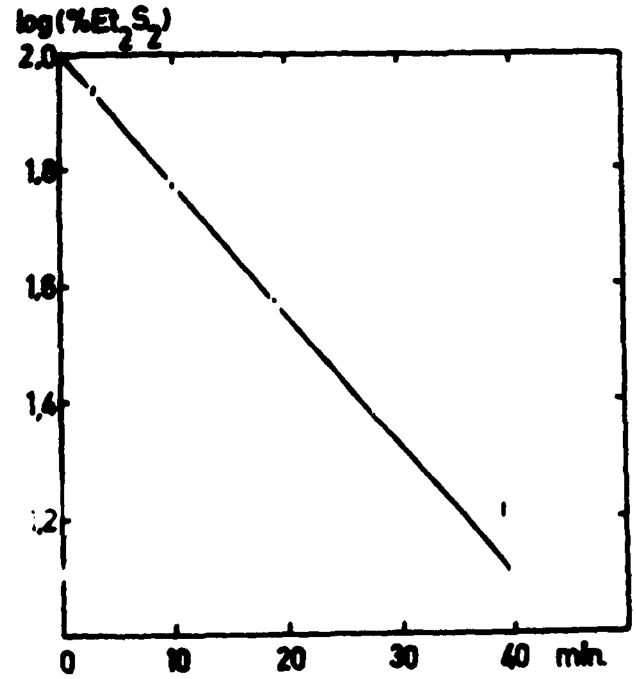
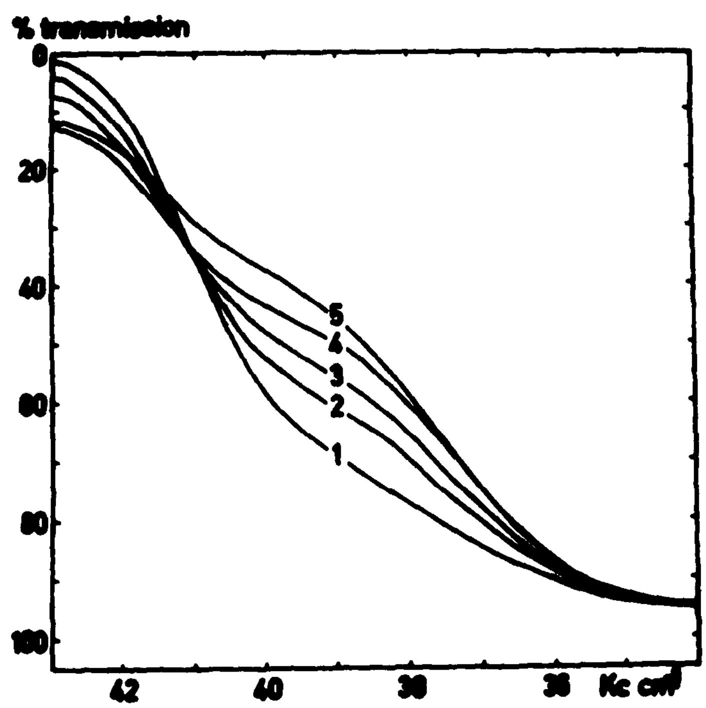


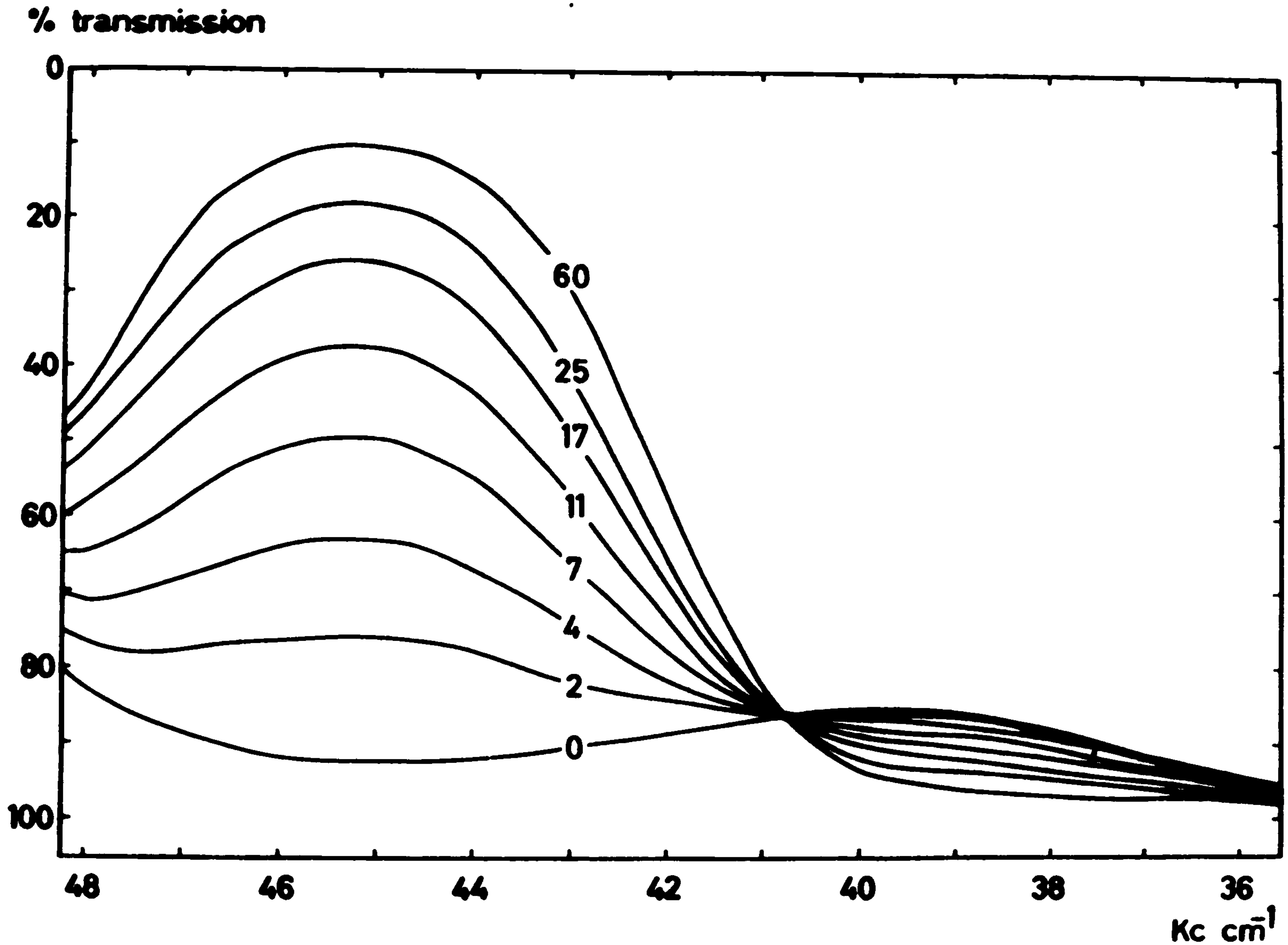
Fig. 3. Photolysis of 0.4 mM n-butyl disulfide in matrix "A" at 77°K. The figures give the time of photolysis in minutes.



<u>Fig. 4.</u> Log (% remaining n-butyl disulfide) from photolysis in matrix "A" at 77°K, plotted against time of irradiation.



<u>Fig. 5.</u> Spectral changes of a 0.4 mM n-butyl disulfide, photolyzed at 77°K and brought to room temperature. After (1) 6 min., (2) 15 min., (3) 30 min., (4) 3 hours and (5) 24 hours at 298°K.



<u>Fig. 6.</u> Photolysis of 0.05 mM n-butyl disulfide in matrix "A" at 77°K. The figures give the time of photolysis in minutes.

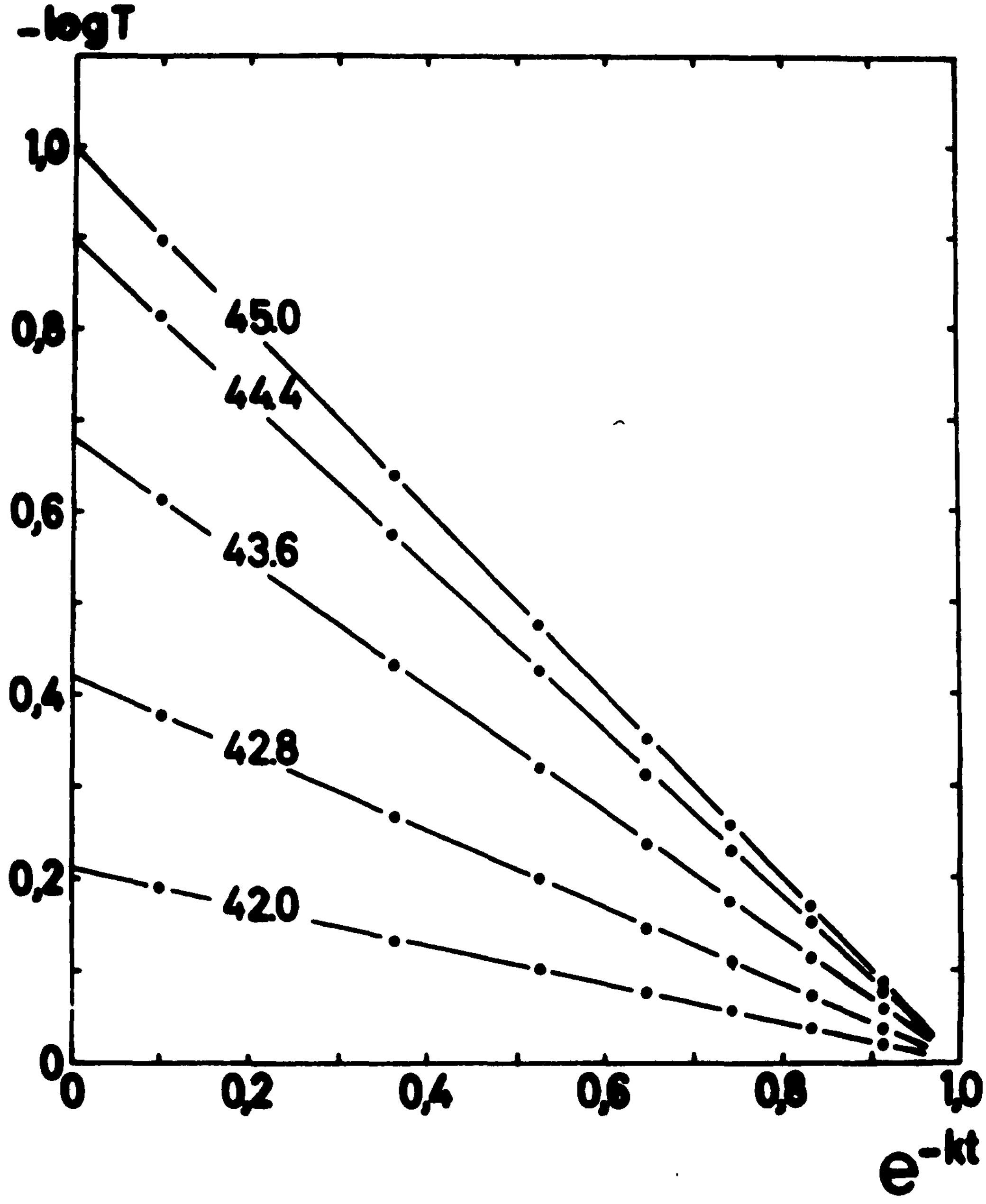


Fig. 7. Optical density plotted against e^{-kt} for various wave-numbers, indicated by figures; k equal to 0.046 min^{-1}.

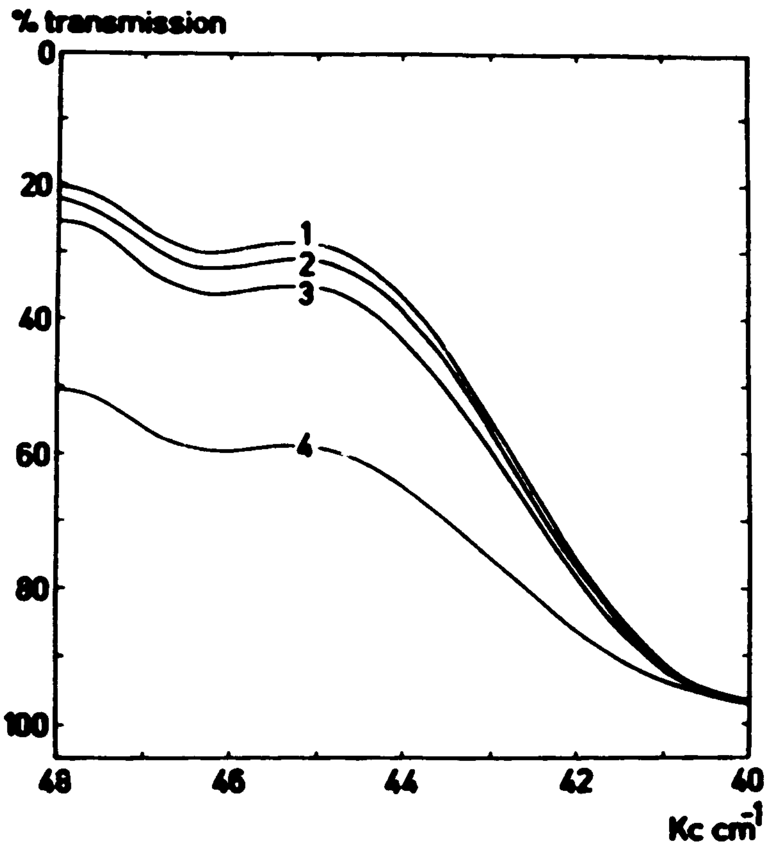


Fig. 9. Spectral changes of a 0.05 mM n-butyl disulfide, photolyzed at 77°K and brought to room temperature. After (1) 5 min., (2) 60 min., (3) 2.5 hours and (4) 18 hours at 298°K.

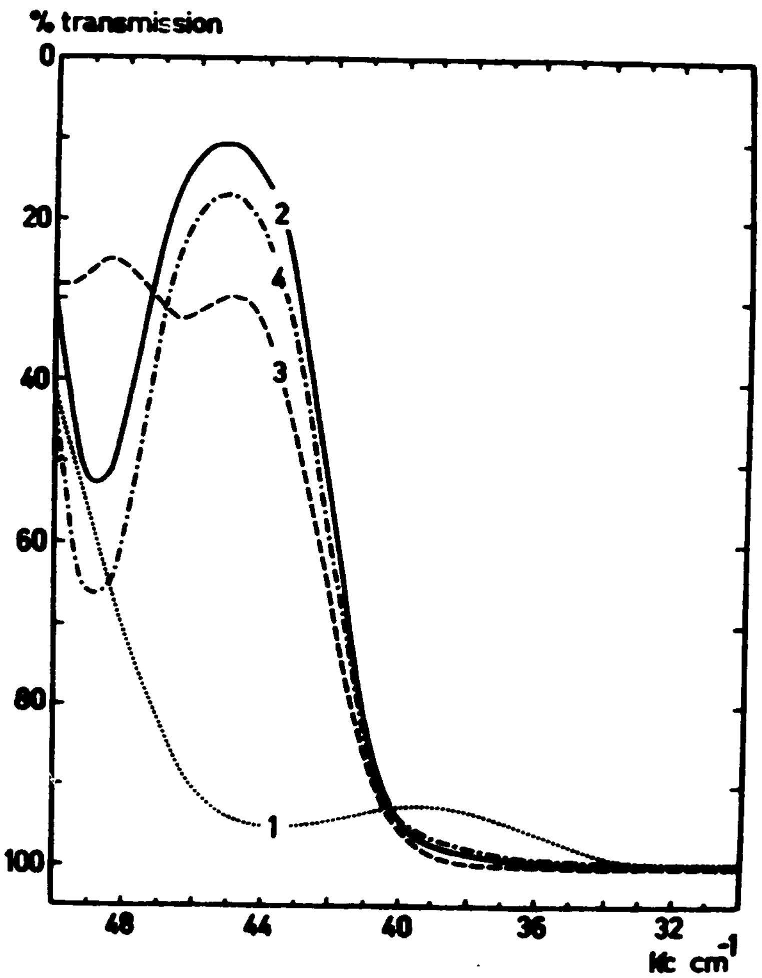


Fig. 8. Spectra of 0.05 mM n-butyl disulfide in matrix "A". (1) Unphotolyzed at 77°K; (2) after 60 min. of photolysis at 77°K and (3) at 298°K; (4) after recooling to 77°K.

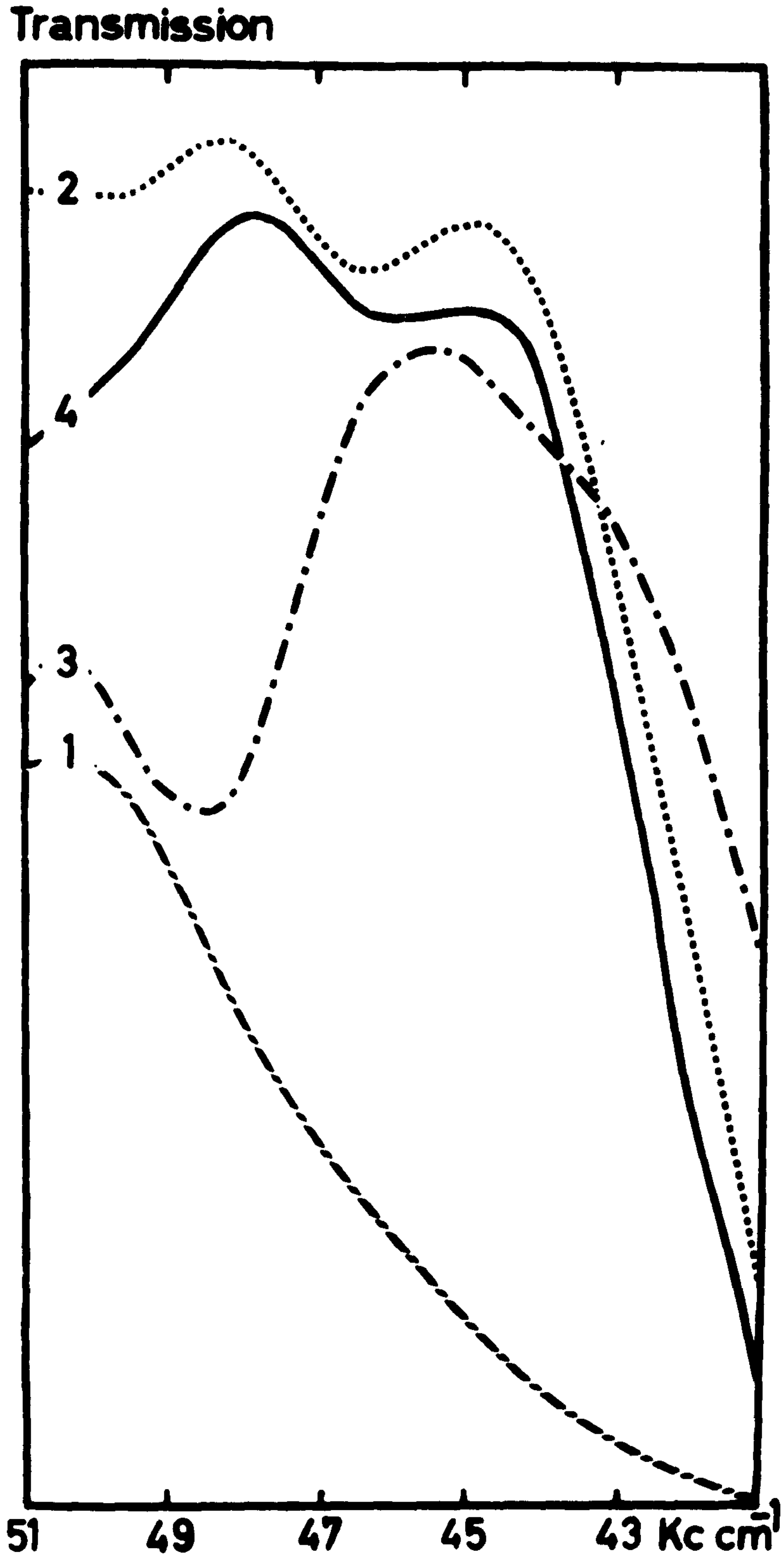
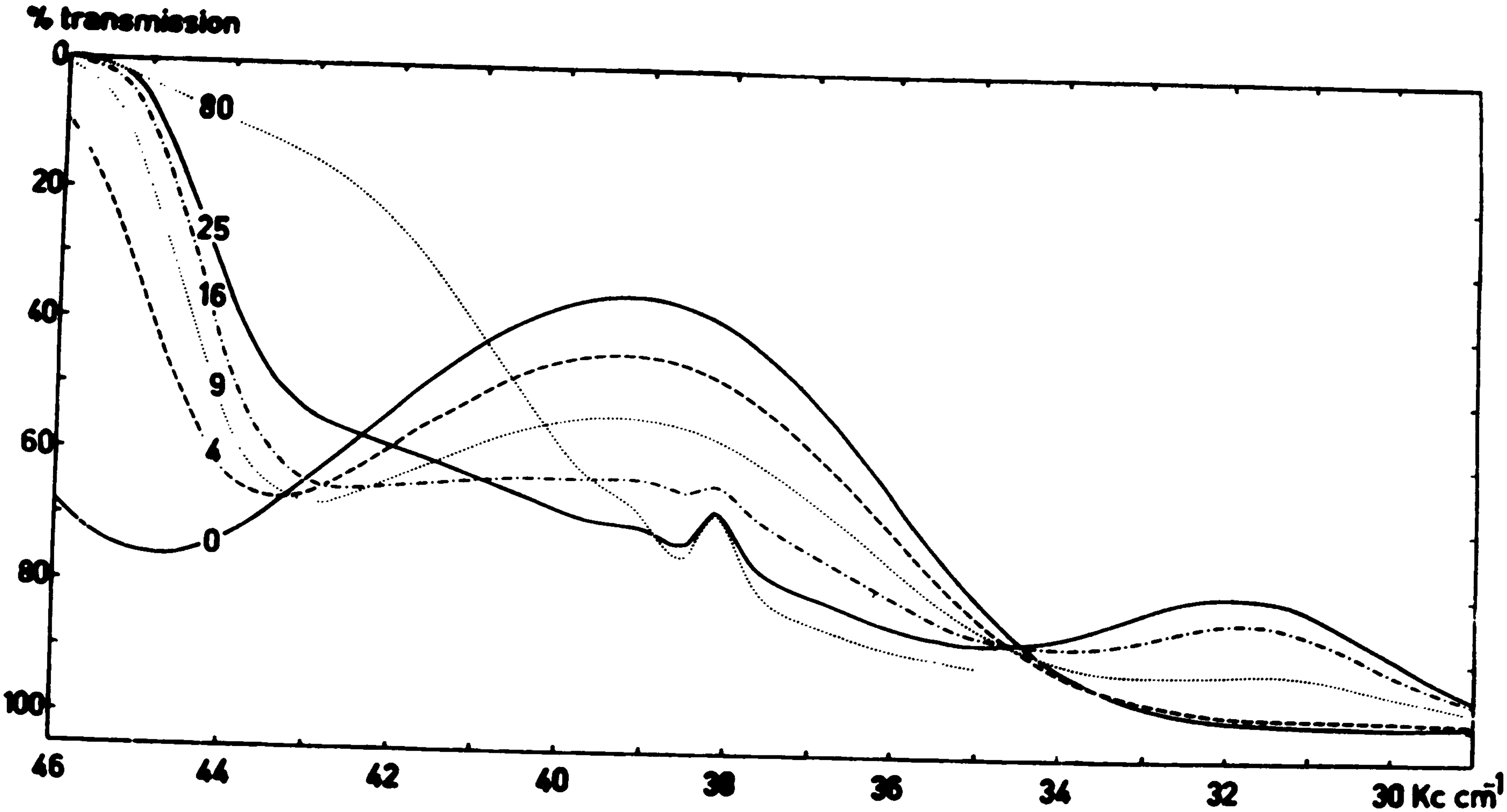


Fig. 10. Spectra of photolyzed disulfides, after warm up. (1) Me_2S_2; (2) n-Bu_2S_2; (3) sec.-Bu_2S_2 and (4) neopentyl disulfide. The 100 % line different for the various disulfides.



<u>Fig. 11.</u> Photolysis of 0.5 mM methyl disulfide in matrix "A" at 77°K. The figures give the time of photolysis in minutes.

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TECHNICAL NOTE

THE PHOTOLYSIS OF ALKANETHIOLS IN A RIGID GLASS AT 77°K WITH THE POSSIBLE FORMATION OF THIYL RADICALS

By

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ABSTRACT: The photolysis of diethyl-, di-i-propyl-, and di-n-butyl disulfide in an organic matrix at 77°K leads to the formation of a rather sharp and fairly stable absorption peak at about 25 kc. cm^{-1}. After warm-up to room temperature, considerable quantities of disulfide were found in the solution. From this and additional experimental evidence, it is concluded that this peak best can be assigned to the thiyl radical.

It has been repeatedly suggested that UV-irradiation of a disulfide leads to the formation of intermediate thiyl radicals (for the literature see e.g. Ref. 1). In an attempt to trap thiyl radicals by photolysis in an organic matrix at liquid nitrogen temperature it has been demonstrated that no such trapping occurred as could be detected by UV-spectrophotometry[1]. As an explanation it has been suggested that the negative result is due to the cage-effect[Ref. 2 p. 95] - that is, the excited thiyl radicals formed in the initial chemical process were unable to separate and therefore reacted according to

$$R_1R_2CHSSCHR_1R_2 \longrightarrow R_1R_2CS + HSCHR_1R_2$$

where R_1 = H, Alk and R_2 = Alk.

Porter et al.[3,4] have reported the successful trapping of a number of radical species by the photolysis reaction $RXH \longrightarrow RX\cdot + H$ utilising the fact that hydrogen atoms easily diffuse through the organic matrix even at 77°K. Consequently, photolysis of an alkane thiol might lead to the desired result - formation of a thiyl radical.

RESULTS

The apparatus and technique used have been described elsewhere[5,6]. Ethanethiol, 2-propanethiol and 1-butanethiol, all of satisfactory purity as judged from GLC, were used in the experiments. iso-Pentane and 3-methyl pentane, 6:1, were used as a matrix-forming mixture. The primary and secondary mercaptans exhibit a weak UV-absorption (ε ca. 150) at 43 kc.cm^{-1}, for 0.05 and 5 mM solution the transmission is 100 % below 40 and 34 kc.cm^{-1}, respectively. In the paper cited[1], control photolysis were performed on 0.4 mM 1-butanethiol using WG7 filters. The main change in spectrum during photolysis was a pronounced increase in transmission between 50 and 46 kc.cm^{-1}.

However, when the photolysis was carried out on 5 mM solutions, all other conditions being equal, the results were as given in Figure 1. Curve 1 shows the spectrum at 77°K before photolysis. Curve 2 was recorded immediately after 10 min. of irradiation. When the sample cell was left at 77°K, curves 3 and 4 were recorded after 30 and 60 minutes, respectively.

The decrease of the 24.6 kc.cm^{-1} peak is evident as is the formation of an isosbestic point at 28 kc.cm^{-1}. When the irradiation was prolonged no further increase of the peak occurred, probably because the increase in ultraviolet absorption above 30 kc.cm^{-1} prevented fur er photolysis of the mercaptan molecules.

When the cells were lifted up from the liquid nitrogen an uneven distribution of the yellow color (24.6 kc.cm^{-1} peak) was observed, the layers near the windows being most strongly colored. The color disappeared when the cell content lost its rigidity and no traces of the peak could be seen at room temperature (curve 5); nor did it appear again when the sample was cooled in liquid nitrogen for a second time. Similar experiments performed with ethanethiol and 2-propanethiol gave analogous results, the absorption peak occurring at 25.6 and 24.8 kc.cm^{-1}, respectively.

The following experiment was performed to show the existence of thiyl radicals in the photolyzed glass. A 5 mM ethanethiol solution photolyzed at 77°K was evaporated slightly above room temperature under a stream of nitrogen. An equal amount of the unphotolyzed solution was treated in exactly the same way. After the solutions had been reduced to about a hundredth of the initial volume, samples were withdrawn, put on the gas chromatograph and analyzed for ethyl disulfide. The photolyzed sample gave a large disulfide peak, whereas it was totally absent in the control experiment.

DISCUSSION

The experimental results strongly indicate that the 24.6 kc. cm^{-1} peak should be assigned to the butylthiyl radical. It is commonly supposed that larger molecular species do not migrate in the hydrocarbon glasses at 77°K[Ref. 2 p. 78] and moreover in the preceding paper it was shown that alkyl disulfides like methyl disulfide did not diffuse to a detectable extent. Therefore, it can safely be assumed that disulfide cannot be formed in considerable amounts at 77°K by photolysis of a mercaptan. The correspondence between the irreversible disappearance of the 24.6 kc. cm^{-1} peak during warm-up and the simultaneous formation of disulfide lead to the natural conclusion that thiyl radicals were present at 77°K and to the assignment of the 24.6 kc. cm^{-1} peak. The slow decrease of the peak at 77°K must be caused by an unknown reaction. The position of the isosbestic point, at 28 kc. cm^{-1}, conclusively rules out both recombination reactions $2RS\cdot \longrightarrow R_2S_2$ and $RS\cdot + H \longrightarrow RSH$. Neither the disulfide nor the mercaptan exhibit any absorption at this low wavenumber.

The splitting of the mercaptan leads to the formation of hydrogen atoms. It has been shown that hydrogenation of the glass-forming i-pentane - 3-methyl pentane mixtures used in this laboratory lead to a minor significant decrease in light absorption at wavenumbers around 48 kc. cm^{-1} [7]. This may be explained by assuming that minute quantities of unsaturated compounds were present as impurities. In this connection, it is of interest to quote Potts[8], who pointed out that i-pentane on standing developes an absorption at 48 to 49 kc. cm^{-1}. It is suggestive to ascribe the decrease in absorption found during the photolysis of the mercaptans in the 50-46 kc. cm^{-1} region to a hydrogenation of olefinic impurities by the hydrogen atoms liberated in the propsed reaction.

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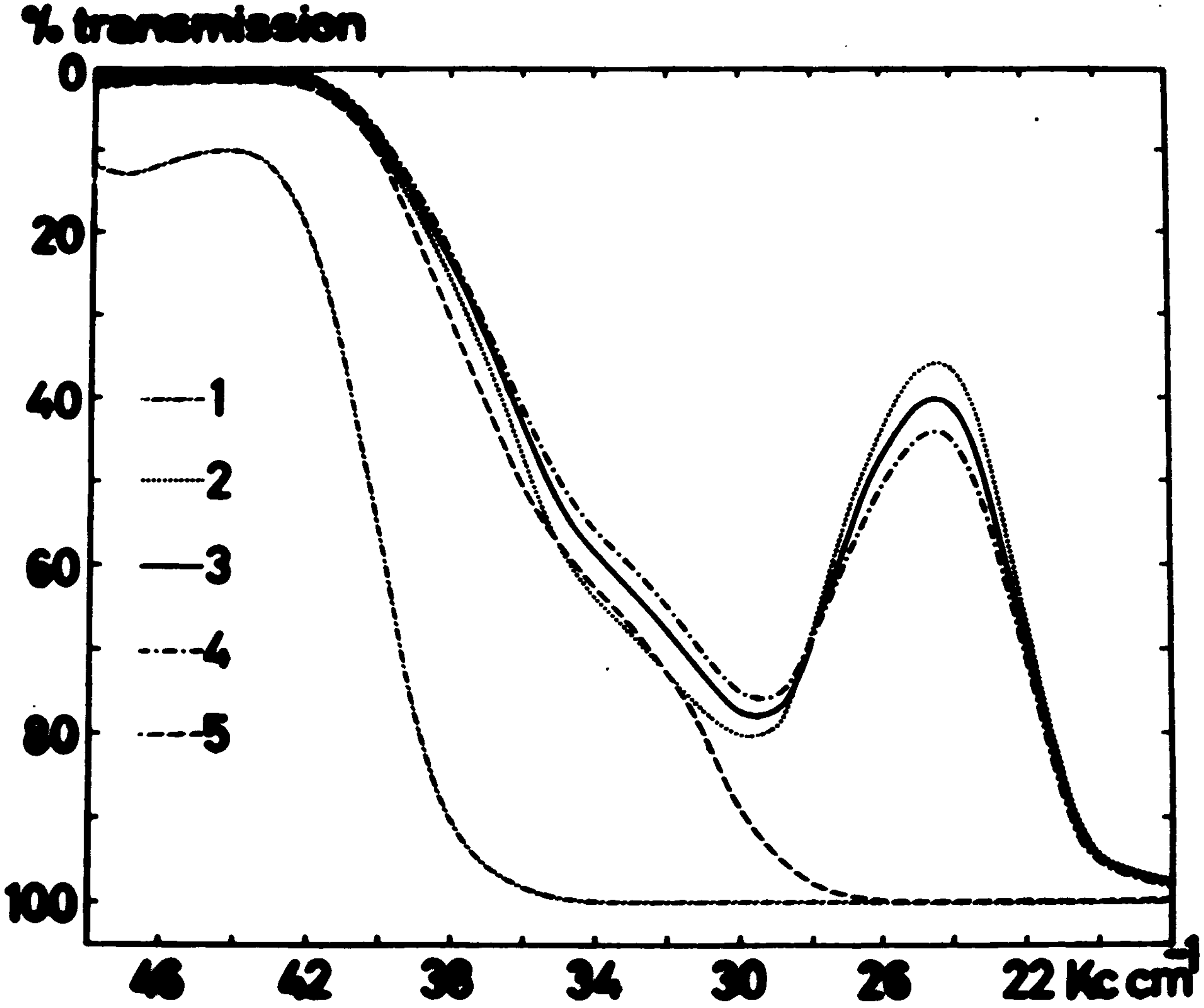

Fig. 1. Photolysis of n-BuSH in matrix A. (1) before photolysis at 77°K, (2) immediately after 10 min. of photolysis, (3) 30 and (4) 60 min. after the end of photolysis. (5) at 298°K.

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TECHNICAL NOTE

THE PHOTOLYSIS OF IODINE, ETHYL IODIDE AND HYDROGEN IODIDE IN A RIGID GLASS AT 77°K

By

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15 January 1962

The research reported in this document has been sponsored by DIRECTORATE OF CHEMICAL SCIENCE, AFOSR, AFRD of the AIR RESEARCH AND DEVELOPMENT COMMAND, UNITED STATES AIR FORCE, through its European Office.

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ABSTRACT: It has been found that the photolysis of iodine in a hydrocarbon matrix at 77°K does not lead to the formation of iodine atoms. That the photolysis of ethyl iodide depends on the viscosity of the matrix has been confirmed and spectral characteristics of intermediates have been recorded. Identical characteristics were found when HI was photolyzed and it has been shown that HI_3 is not involved.

INTRODUCTION

In a search for molecular species that can be split homolytically by photolysis in a glass-forming matrix at the temperature of liquid nitrogen a number of iodine-containing substances have been investigated. The photolysis of iodine, ethyl iodide and hydrogen iodide constitutes the subject of the present paper.

Iodine itself has previously been studied by Norman and Porter[1,2] and by Sowden and Davidson[3] under similar conditions but with controversial results. Norman and Porter[1] found it possible by photolysis to decolorize a 10^{-3} M iodine solution in a hydrocarbon glass at 86°K and to regain the iodine color during warm-up. On the other hand, Sowden and Davidson[3] found a 10^{-4} M solution to be unchanged even by prolonged irradiation. In a later paper, Norman and Porter[2] described the experimental conditions and results more in detail when using the EPA-matrix (ethanol, ethyl ether and iso-pentane 2:5:5).

Norman and Porter[2] have also studied the photolysis of EtI in different matrices. These authors suggested that atomic iodine was formed, which is stable at 77°K for several hours in a high-viscosity, "hard" matrix like pure 3-methyl pentane or the mixture 3-methyl pentane, iso-pentane 3:2, whereas in a low-viscosity, "soft" matrix like pure iso-pentane diffusional processes lead to the formation of molecular iodine already at liquid nitrogen temperature. Upon warm-up the spectrum of iodine appeared instantly also in hard glasses. In EPA, the authors found that the solid solution irradiated for 1 hour remained transparent down to the beginning of absorption by EtI. On warming to room temperature, the absorption spectrum of iodine developed rather slowly, showing also the absorption bands at 290 and 360 mμ attributed to hydrogen tri-iodide[4]. Norman and Porter concluded that the photolysis of EtI leads to the formation of unknown species, which may be HI. They do not give any corresponding results when hydrocarbon matrices were used.

It was felt to be of interest to repeat the photolysis of ethyl iodide with a differential method on a hydrocarbon matrix and to compare the results with those from experiments performed on hydrogen iodide under identical conditions.

MATERIALS

Iodine used was "Baker analyzed" reagent.

Ethyl iodide, Merck analytical grade, was distilled and the main fraction was found to contain less than 0.05 % of gas-chromatographically detectable impurities.

Hydrogen iodide was prepared directly in a 10^{-3} M hydrocarbon solution by reduction with pure hydrogen of an appropriate amount of iodine in the presence of 10-20 % by weight of platinum oxide (Adams catalyst[5]).

Matrix hydrocarbons were purified and tested according to standard procedure[6].

Apparatus and Technique have been described elsewhere[7-8].

EXPERIMENTAL RESULTS

Iodine. (Figure 1) Iodine solutions (1.5×10^{-5} to 4×10^{-5}) M[x] were prepared in three different glasses: two mixtures of iso-pentane and 3-methyl pentane, 2:3 by volume[2] (matrix C) and 6:1 by volume[9] (matrix A) and a mixture of n-pentane and neohexane 3:8 by volume[10] (matrix B). The solutions were cooled to liquid nitrogen temperature (curve 1) and irradiated for 60 minutes (curve 2). All glasses were yellow and fully transparent in the visible region throughout the experiments. The peaks at 19.9 and 23.0 kc. cm^{-1} were clearly discernible both before and after photolysis. In accordance with the results of Sowden and Davidson no decolorization was obtained, and the spectrum changed only slightly or not at all during the irradiation. After warm-up, the original spectrum was obtained, within the error of reproducibility of the instrument (curve 3). On refreezing, however, the spectrum differed slightly from the unirradiated one at 77°K (curve 4).

---

[x] Above ca. 10^{-4} M, the solution became turbid upon freezing.

<u>Ethyl iodide</u> was irradiated at liquid nitrogen temperature in all three matrices given above at concentrations between 10^{-3} and 10^{-4} M. The spectral changes following upon irradiation depended on the viscosity of the matrix[x]. In the high-viscosity matrix, C (Figure 2a), the absorption peak at 38.9 kc. cm^{-1} (curve 1) decreased regularly during the initial 15-20 minutes of photolysis. At the same time the absorption at higher frequencies increased whereas the curve is unchanged at lower frequencies. The curves for different photolysis times cross each other in an isosbestic point at about 42.4 kc. cm^{-1}.

For longer irradiation periods, up to 60 minutes, the absorption increased over the whole UV-region with a recognizable peak at about 23 kc. cm^{-1} (curve 2). This spectrum remained unchanged as long as long as liquid nitrogen surrounded the cell. If the sample was slowly warmed up when still in the cell compartment, the following changes in the spectrum occurred:
A weak maximum appeared at 13.9 kc. cm^{-1}, a strong double peak at 25.8 and 27.4 kc. cm^{-1}, respectively, and a peak at 34.4 kc. cm^{-1} (curve 3). When room temperature was reached the spectrum showed only the presence of iodine: a peak at 19.1 kc. cm^{-1} and an increased absorption in the far UV-region (curve 4). Refreezing to liquid nitrogen temperature, however, did not result in the spectrum of an iodine solution at $77^{o}K$ (Figure 1, curve 1); the absorption below about 30 kc. cm^{-1} is lower and above this point higher for the irradiated sample than it is for iodine (curve 5). Besides, a new peak appeared at 22.3 kc. cm^{-1}, which might be an indication of the formation of HI_3 (see below).

In the other matrices spectral changes occurred already during irradiation when the cells were surrounded by liquid nitrogen. Figure 2b, curve 1 shows the absorption of a 0.25 mM EtI solution in matrix A at $77^{o}K$. After 5-10 minutes of irradiation a peak developed at 25.8 kc. cm^{-1} and at about 21 kc. cm^{-1} (curves 2 and 3). On prolonged irradiation peaks at 27.4 and 34.4 kc. cm^{-1} developed faster than the 25.8 kc. cm^{-1} peak, so that the final spectrum at $77^{o}K$ (curve 4) was similar to that obtained in matrix C. Fifteen minutes of photolysis of EtI in matrix B gave rise to peaks at 25.6, 27.5 and 34.4 kc. cm^{-1} and a shoulder at about 21 kc. cm^{-1} - that is, the same characteristic frequencies as in the chemically different matrices A and C.

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x) For an experimental study of the viscosity of the different matrices see Ref. 6.

Hydrogen iodide. At room temperature, hydrogen iodide has an absorption maximum at 37.4 kc. cm^{-1} (Figure 3) in the hydrocarbon mixtures used (curve 1). At liquid nitrogen temperature this maximum is changed to 36.7 kc. cm^{-1} and a new weaker maximum appears at 32.1 kc. cm^{-1} (curve 2).

Hydrogen iodide was irradiated in matrices A and B at concentrations between 2×10^{-4} and 4×10^{-4} M. In the harder matrix C, only one experiment could be performed as the cells almost invariably broke during photolysis. In both glasses the two HI absorption peaks rapidly decreased upon irradiation; after about 10 min. they had practically disappeared. The changes in spectrum as a result of the irradiation were quite analogous to those obtained with ethyl iodide. Thus, the final spectrum at low temperature was dominated by a peak at 34.4 kc. cm^{-1} and a double-peak at 27.4 and 25.8 kc. cm^{-1} (curve 3). After warm-up the spectrum was again that of iodine (curve 4) and after refreezing the spectrum resembled that of irradiated ethyl iodide under the same conditions, with a peak at 22.7 kc. cm^{-1} (curve 5).

Hydrogen iodide and iodine. (Figure 4) Solutions were prepared in matrix A containing both hydrogen iodide (about 4×10^{-4} M) and iodine (about 3×10^{-5} M). At room temperature the spectrum showed the absorption of both compounds. At 77°K, however, the spectrum did not consist of superimposed spectra of hydrogen iodide and iodine (curve 2). The excess HI could easily be identified on a high absorption background with peaks at 36.7 and 32.1 kc. cm^{-1}. Contrary to this the low temperature absorption of iodine in the wavenumber range 28-18 kc. cm^{-1} was absent and a new sharp peak had developed at 22.1 kc. cm^{-1}. Irradiation of this mixture gave the same spectral changes as a hydrogen iodide solution alone (curve 3).

DISCUSSION

Upon freezing the violet iodine-solution in a hydrocarbon mixture solidified to a yellow, transparent glass, the color change being caused by an increase in light absorption for wavenumbers higher than about 20 kc. cm^{-1}. It has been suggested that the cause may be the low solubility of iodine at $77^{o}K$. An extrapolation made by Ham[11] led to an order of magnitude of 10^{-11} M and thus the color of the solution should be caused by microcrystals of iodine. Evans[12] has pointed out that the iodine solution may be colloidal and that Norman and Porter[1], who were able to prepare a transparent 10^{-3} M solution of iodine, probably used solvents containing impurities which formed complexes with I_2.

The existence and the reproducibility of the 23.0 and 19.9 kc. cm^{-1} peaks show that certain complexes between iodine and solvent molecules must be present in all matrix-forming hydrocarbon mixtures and that the peaks probably are superimposed on a continuous background absorption. It may be the presence of complex-forming impurities in the solvents or the formation of contact charge transfer complexes[13,14] that give rise to the peaks.

From the irradiation experiments it was apparent that iodine did not photolyze under the conditions chosen. The 23.0 kc. cm^{-1} peak, which did not change very much upon photolysis, disappeared, however, after warm-up followed by refreezing. This could simply be explained by assuming that a type of minor impurity present in both glass-forming mixtures reacts during warm-up.

The absorption curves for HI compared with those for the HI-I_2-mixture clearly demonstrated the existence of a complex between HI and I_2 at $77^{o}K$ with an absorption peak at 21.9 kc. cm^{-1}. Both the photolyzed solution of HI as well as that of EtI showed the formation of I_2 upon warm-up and the same peak became visible upon refreezing at 22.4 and 22.3 kc. cm^{-1}, respectively (corrected for the background absorption).

In the experiments with EtI the influence of the viscosity of the matrix was clearly demonstrated. In the hard matrix, C, the EtI-peak at 38.9 kc. cm^{-1} diminished continuously during rather short times of photolysis without a simultaneous formation of intermediates, which produce a higher absorption below 42.4 kc. cm^{-1} than EtI itself. From the observations of Norman and Porter[2] it seems clear that photolysis occurred during the formation of iodine atoms and ethyl radicals. For longer

irradiation periods the continuously increasing absorption when going towards higher wavenumbers might be caused by secondary irradiation processes[x)].

When the photolyzed EtI solution in matrix C was slowly warmed up the same change occurred as in matrices A and B at 77°K, although distinct differences also were apparent. The spectral changes indicated a sequence of reactions and most probably the formation of more than one intermediate species, showing absorption maxima at 34.4, 27.4, 25.8 and 13.9 kc. cm^{-1}. That the photolysis of HI leads to the formation of the same absorption peaks must have a profound bearing upon the nature of the intermediate products. It therefore seems that they all are related to iodine-containing intermediates and that they have very little, if anything, to do with the existence of a HI_3 complex (cf. Figure 4). It is of interest, however, to note that the well-known peaks produced by an ethanolic iodine-solution, at 34.5 and 27.8 kc. cm^{-1}, have been attributed to HI_3 by Batley[4], and that the 34.4 and 27.4 kc. cm^{-1} peaks obtained when EtI and HI are photolyzed develop simultaneously.

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x) The optical properties of the solid solutions in the different matrices showed quite a variation at 77°K. EtI in matrix C gave a rather high background absorption (Figure 2a, curve 1). In spite of this, the spectral changes could very well be reproduced although calculations of extinction coefficients became too uncertain to be of value.

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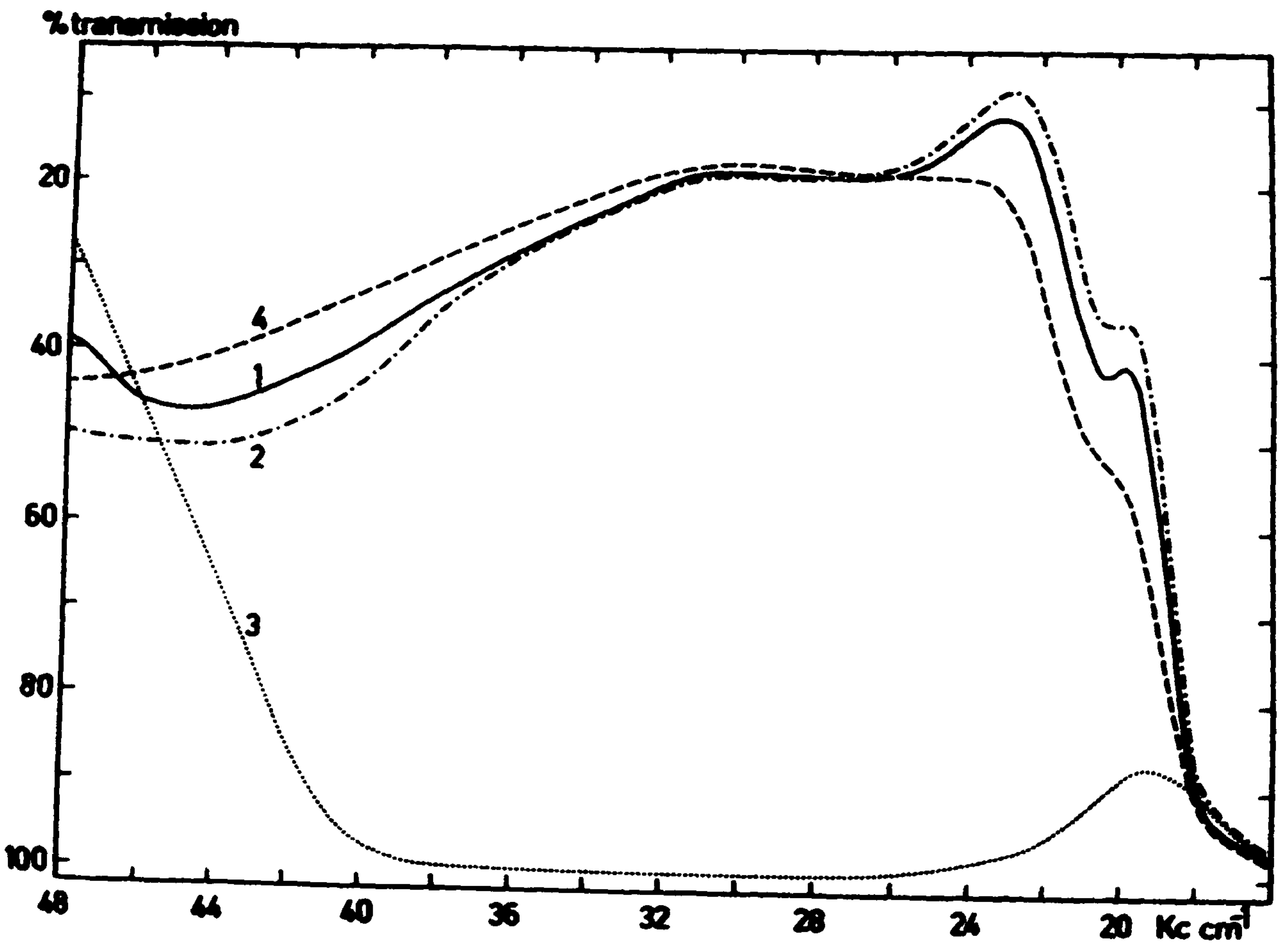


Fig. 1. Spectra of a 3×10^{-5} M iodine solution in matrix A. (1) before and (2) after 60 min. of photolysis at 77^oK, (3) after warm-up to 298^oK and (4) after recooling to 77^oK.

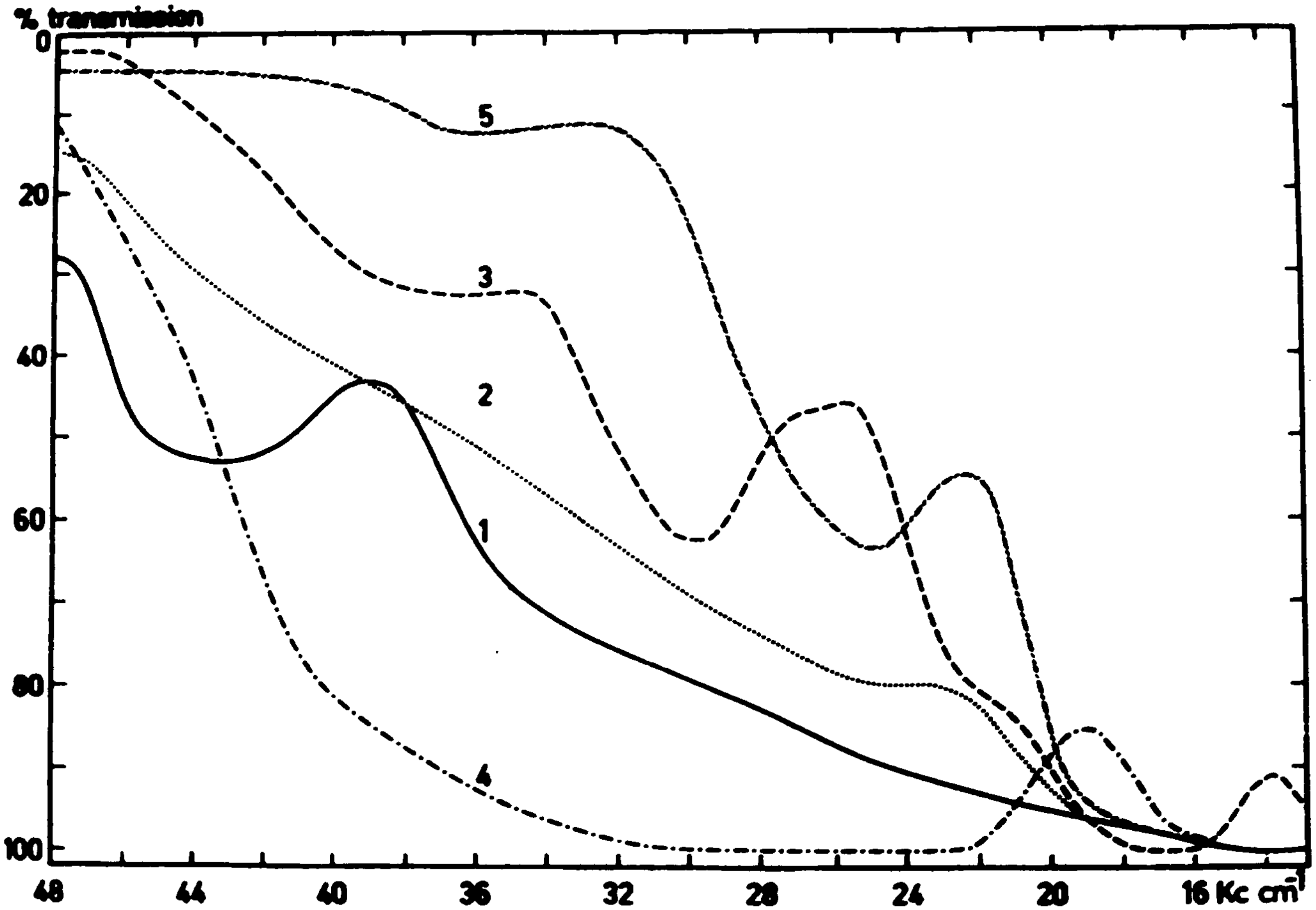


Fig. 2a. Spectra of a 2.5×10^{-4} M ethyl iodide solution in matrix C. (1) before and (2) after [illegible] min. of photolysis at 77°K, (3) during warm-up, at approximately [illegible] °K, [illegible] after [illegible] to 298° K and (5) after recooling to 77°K.

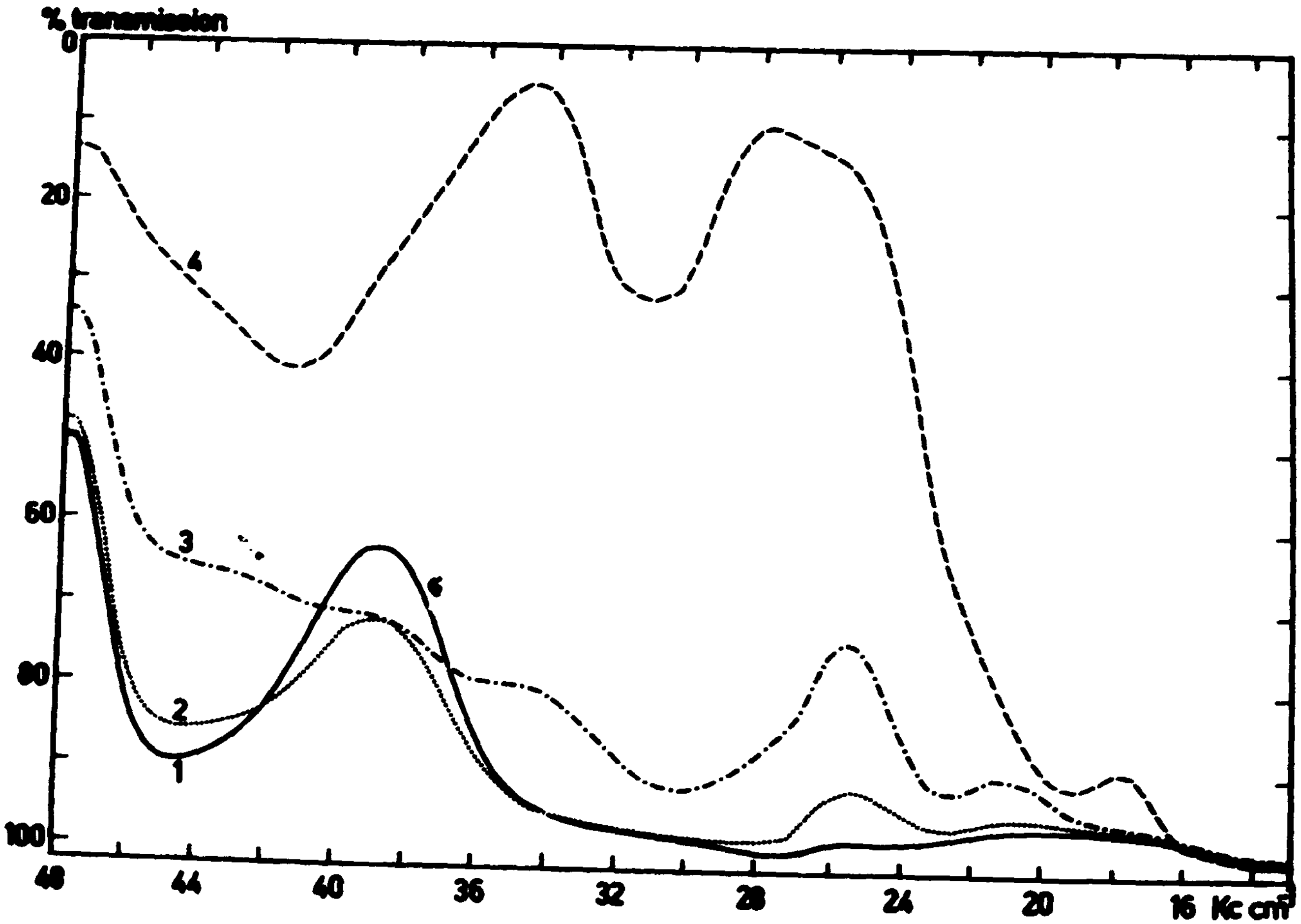
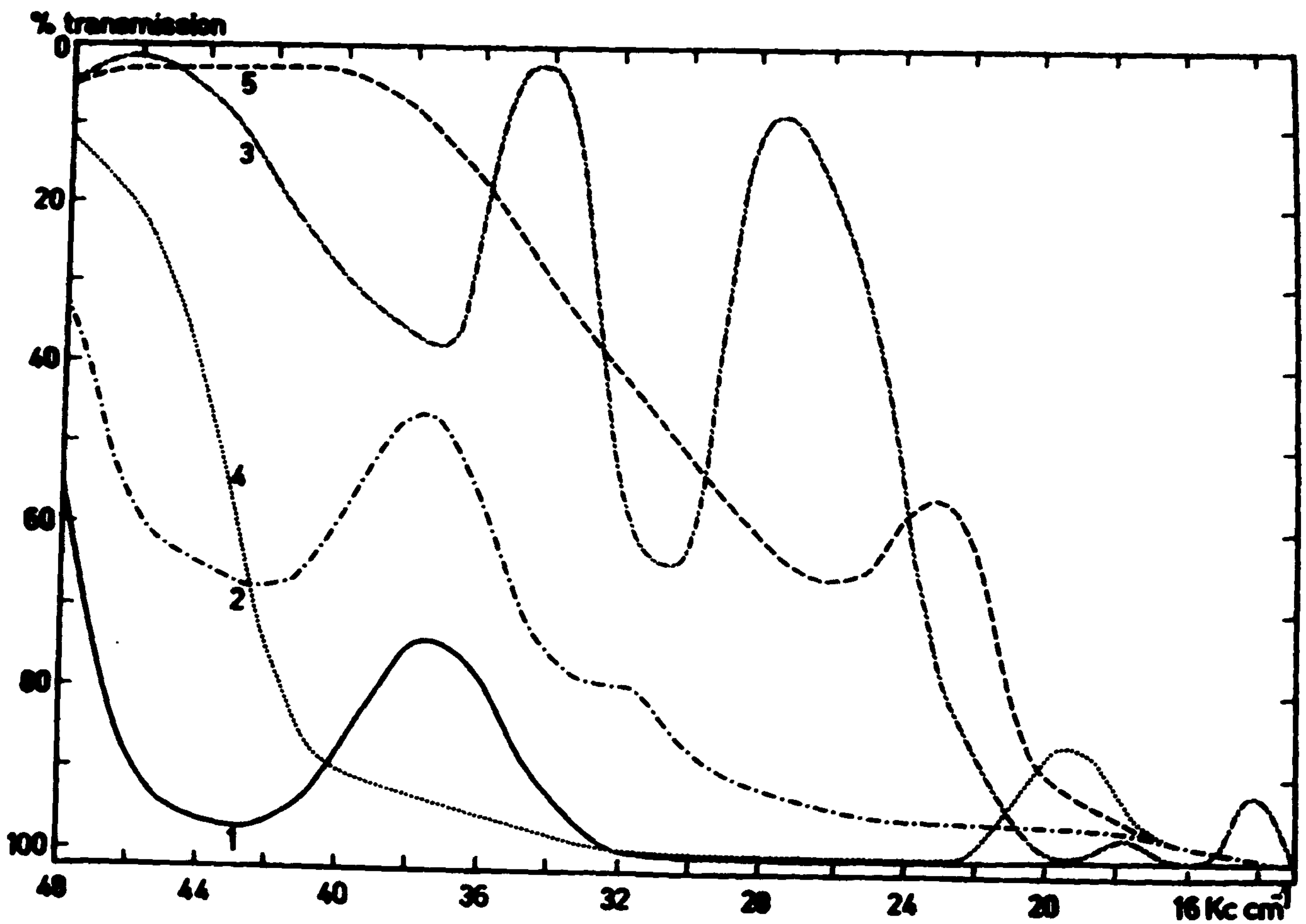


Fig. 2b. Spectra of a 2.5×10^{-4} M ethyl iodide solution in matrix A at 77°K. (1) before and after (2) 5 min., (3) 12 min. and (4) 30 min. of photolysis.



<u>Fig. 3</u>. Spectra of 1.9×10^{-4} M hydrogen iodide solution in matrix A. (1) at 298°K, (2) before and (3) after 60 min. of photolysis, (4) after warm-up and (5) after recooling to 77°K.

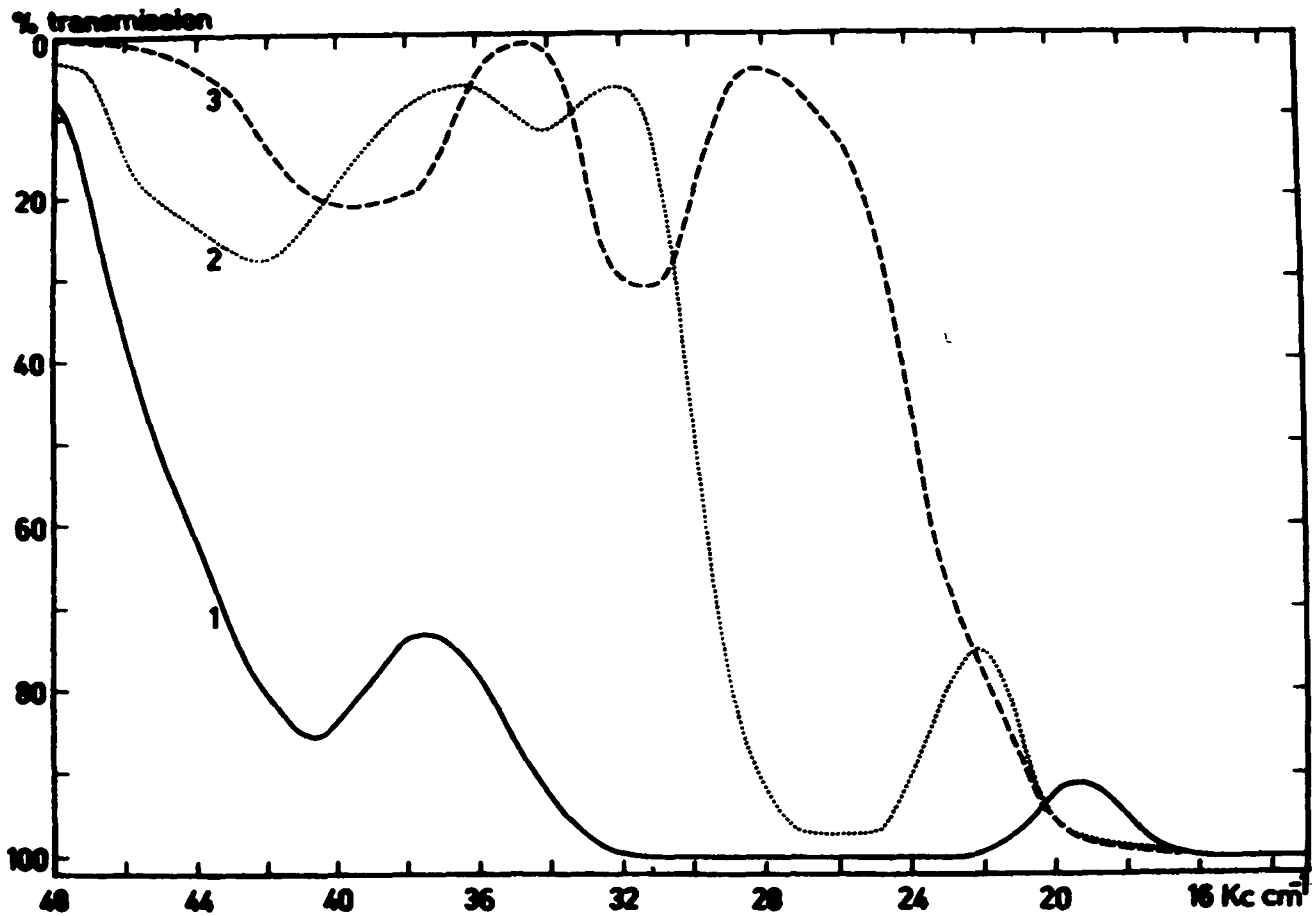


Fig. 4. Spectra of a mixture of 4×10^{-4} M hydrogen iodide plus 3×10^{-5} M iodine in matrix A solution. (1) at 298°K, (2) before and (3) after 10 min. of photolysis at 77°K.

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ABSTRACT cont.

All primary and secondary disulfides (except Me_2S_2) behave in an analogous stoichiometrically simple way (in contrast to tert. butyldisulfide). Strong evidence is presented for the view that the only detectable over-all reaction occurring during photolysis is

$$R_1R_2CHSSCHR_1R_2 \longrightarrow R_1R_2C{=}S + HSCHR_1R_2.$$

The presence of both reaction products has been established.

The spectral changes during the photolysis of dimethyl disulfide are only initially analogous to those of the other primary disulfides. Upon prolonged irradiation unknown reactions occur, leading to the formation of carbonmonosulfide, CS, among other products.

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